The Preparation and Decomposition of Tetrathionates

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DISSERTATION

PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE SCHOOL OF THE OHIO STATE UNIVERSITY

BY

WALTER SCOTT

THE OHIO STATE UNIVERSITY
1920

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INTRODUCTION

Tetrathionates and tetrathionic acid were first prepared by Fordos and Gelis in 1842. They were making anaylses of a great number of commercial salts, then called "hyposulphites," in order to see if they had the same composition.

In the course of the analysis they attempted to oxidize a solution of the salts with iodine in order to convert the sulphur to sulphate. Instead of forming a sulphate, a new compound of sulphur was formed and which proved on analysis to have the general formula $M''S_4O_6$. Since the discovery of the tetrathionates much work has been done on them and the results obtained are not in agreement. The principal reason for this seems to be that the tetrathionates were prepared from Wackenroder's solution, which was not of uniform composition.

The object of the present investigation was to get some definite data on some of the tetrathionates, and to further study their decomposition quantitatively under the same conditions.

SODIUM TETRATHIONATE

BIBLIOGRAPHY

Fordos and Gelis, *Ann. Chim. phys.*, (3) **6**, 486, (1842).
Jour. f. prak. Chem., **28**, 473, (1843).
Compt. rend., **2**, 920, (1843).

Sodium tetrathionate was prepared by the action of sodium thiosulphate on iodine. The sodium thiosulphate was dissolved in water and the iodine added a little at a time until there was a slight iodine color remaining. They also stated "That the liquid contained neither sulphates, sulphuric acid nor any salt which is precipitated by baryta."

Fordos and Gelis, *Ann. chim. phys.*, (3) **8**, 351, (1843).

Sodium tetrathionate was prepared by the action of ferric chloride on sodium thiosulphate.

$$2Na_2S_2O_3 + 2FeCl_3 = 2FeCl_2 + 2NaCl + Na_2S_4O_6$$

All ferric salts behave in a similar way.

Fordos and Gelis, *Ann. chim. phys.*, (3) **13**, 402, (1845).

Sodium tetrathionate was prepared by the action of auric chloride on sodium thiosulphate.

Kessler, *Jour. f. prak. Chem.*, **47**, 34, (1849).
Pogg. Ann. Phys. Chem. **74**, 255, (1849).

Sodium tetrathionate was prepared by adding cupric chloride dropwise to a con-

centrated solution of sodium thiosulphate until the cuprous chloride had separated and the solution had a light blue color. It was filtered, and alcohol added to the filtrate whereby the sodium tetrathionate was precipitated.

Kressler also prepared the salt by two other methods.

(*a*) By the addition of an equivalent amount of sodium carbonate to a solution of tetrathionic acid, and then adding alcohol.

(*b*) By mixing equivalent solutions of sodium sulphate and lead tetrathionate, filtering and then adding alcohol.

The tetrathionic acid and lead tetrathionate were prepared by the method of Fordos and Gelis. (*loc. cit.*)

Sonstadt, *Chem. News*, **26,** 99 (1872).

Sodium tetrathionate was prepared by mixing solutions of sodium thiosulphate and potassium iodate and then adding hydrochloric acid.

$$6Na_2S_2O_3 + KIO_3 + 6HCl = 3Na_2S_4O_6 + KI + 6NaCl + 3H_2O$$

Citric and tartaric acids were used instead of hydrochloric and similar results were obtained.

Sonstadt suggests the use of pure sodium thiosulphate to determine pure iodine, as pure iodine will not liberate any sulphur from pure thiosulphate solution.

Lunge, *Ber.*, **12,** 404, (1879).

In experimenting with the action of hypochlorite on thiosulphate, having the thiosulphate in excess, the principal reaction was found to be

$$2Na_2S_2O_3 + Cl_2 = Na_2S_4O_6 + 2NaCl$$

Other reactions occur.

Klobukow, *Ber.*, **18,** 1871, (1885).

Sodium tetrathionate was prepared by the action of iodine on sodium thiosulphate. The sodium thiosulphate was finely pulverized in a mortar and a small amount of water added to make a paste. Finely pulverized iodine was added a little at a time, grinding thoroughly after each addition, until the iodine was in slight excess which may be told by the appearance of the yellow color. Pour the syrupy liquid into a beaker and add alcohol, whereupon the tetrathionate salt is immediately precipitated as a snow-white crystalline precipitate. In case the iodine color disappears during the grinding, a little more iodine should be added until there is a permanent iodine color remaining. By working under the above conditions they believe there was not an excess of alkali thiosulphate present, nor did any decomposition occur liberating sulphur dioxide. After two or three hours standing, the mixture was filtered and the precipitate washed with alcohol until all the iodine and iodide had been removed. The precipitate was dissolved in lukewarm water, reprecipitated by the addition of alcohol, filtered, and placed in a vacuum desiccator over sulphuric acid to dry.

Villiers, *Compt. rend.*, **108,** 402–03, (1889).
Ber., **22,** R. 222, (1889).

Sodium tetrathionate was prepared by passing sulphur dioxide through a solution of sodium thiosulphate.

$$2Na_2S_2O_3 + 3SO_2 = Na_2S_4O_6 + Na_2S_3O_6$$

Norris and Fay, *Amer. Chem. Journ.*, **18,** 703, (1896).

Hydrochloric acid was added to a solution of selenious acid, and then an excess of sodium thiosulphate. The excess of sodium thiosulphate was taken up with iodine.

$$SeO_2 + 4Na_2S_2O_3 = 2Na_2S_4O_6 + Se + 2Na_2O$$

The reaction is quantitative.

Nabl, *Ber.*, **33,** 3554, (1900).

Sodium tetrathionate was prepared by the action of hydrogen peroxide on a solution of sodium thiosulphate.

$$2Na_2S_2O_3 + H_2O_2 = Na_2S_4O_6 + 2NaOH$$

The sodium hydroxide must be removed as soon as it is formed or there is also formed in the solution, sulphite, thiosulphate and sulphate.

He withdraws his previous statement as to the action of hydrogen peroxide on a solution of sodium thiosulphate. *Ber.*, **33,** 3093, (1900).

Nabl, *Monatshefte f. Chem.*, **22,** 737, (1901).

Sodium tetrathionate was prepared in the same way as in the above article. If the alkali is not neutralized, the oxidation of the thiosulphate is only 25% complete and there is also formed dithionate and sulphate as well as tetrathionate.

Willstatter, *Ber.*, **35,** 1831, (1903).

He states that the action of hydrogen peroxide on a solution of sodium thiosulphate is

$$2Na_2S_2O_3 + 4H_2O_2 = Na_2S_3O_6 + Na_2SO_4 + 4H_2O$$

This is in disagreement with the results of Nabl (*loc. cit.*)

Thatcher, *Zeitschr. f. phys. Chem.*, **47,** 641, (1904).

Sodium tetrathionate was prepared by the electrolytic oxidation of sodium thiosulphate in neutral solution, using platinized electrodes with a definite anode potential difference. He considered the reaction to be a secondary rather than a primary one, probably brought about by the oxygen which is formed during the electrolysis together with the aid of the platinized electrodes.

Primary: $2S_2O_3'' + 2F = S_4O_6''$

Secondary: $O'' + 2F = 1/2\ O_2$

$$\tfrac{1}{2}\ O_2 + 2S_2O_3'' = S_4O_6'' + O''$$

Abel, *Monatshefte f. Chem.*, **28,** 1239, (1907).

Sodium tetrathionate was prepared in two ways.

(*a*) By the action of hydrogen peroxide on sodium thiosulphate in acetic acid solution.

$$H_2O_2 + 2Na_2S_2O_3 + 2CH_3COOH = Na_2S_4O_6 + 2CH_3COONa + 2H_2O$$

(*b*) By the action of hypoiodite on thiosulphate in acetic acid solution.

$$IO' + 2S_2O_3'' + 2H' = S_4O_6'' + H_2O + I'$$

Fromm, *Ber.*, **40,** 3397, (1908).

The sodium tetrathionate was prepared by the method of Klobukow (*loc. cit.*). He analyzed the salt by determining the barium sulphate; also by determining the sodium sulphate. The water of crystallization was determined by drying the salt at 110° C.

Stiasny and Das, *Jour. Soc. Chem. Ind.*, **31,** 753, (1912).

Sodium tetrathionate was prepared by the action of potassium dichromate and sulphuric acid on a solution of sodium thiosulphate. They give three possible reactions, but in only one is the tetrathionate formed. The extent to which each of these reactions takes place depends on the dilution and the amounts of acid and thiosulphate present.

Vanino and Schinner, *Ber.*, **46,** 1776, (1914).

Sodium tetrathionate was prepared by the method of Fordos and Gelis (*loc. cit.*).

About 50 grams of pure sodium thiosulphate ($Na_2S_2O_3.5H_2O$) and 25 grams of iodine were finely pulverized in a mortar, placed in a 500 cc. flask and treated with 50 cc. of absolute alcohol. The pasty mass (at the ordinary temperature) was kept in constant motion by means of a shaking machine until complete decolorization, requiring about two days. Pulverized iodine was now added until permanent coloration, and then 100 cc. of absolute alcohol. The separated salt was washed with a mixture of absolute alcohol and ether until the wash liquid after the addition of some water and ammonia no longer became turbid on the addition of silver nitrate. After that the salt was dried in the air between filter paper, then placed in a beaker and dissolved in 50 cc. to 60 cc. of distilled water. A small amount of iodine dissolved in alcohol was added to this solution until there was a permanent coloration of iodine, then 350 cc. of a mixture of absolute alcohol and ether. After standing some time the salt was filtered off, washed with absolute alcohol-ether, and lastly with ether only. In a short time it lost the odor of ether and was then placed in a stoppered bottle.

Sander, *Zeitschr. angew. Chem.*, **28,** 273, (1915).

The tetrathionates of sodium and potassium were prepared by the method of Fordos and Gelis (*loc. cit.*).

26 grams of iodine were dissolved in alcohol and into this cooled solution a saturated solution of 50 grams of sodium thiosulphate ($Na_2S_2O_3.5H_2O$) or 39.5 grams of potassium thiosulphate (at room temperature) were added gradually by means of a drop funnel. The decomposition of the thiosulphate occurs immediately with the excess of iodine, and the tetrathionate which is formed being insoluble in alcohol separates in small crystals. These crystals were filtered off and washed with alcohol until the wash liquid was free of iodine and iodide, then dissolved in the least possible amount of water and reprecipitated by the addition of alcohol. The crystals were filtered off, pressed between filter paper and finally dried over sulphuric acid.

On analysis the potassium salt was found to be pure and the sodium salt to be impure. The methods of analysis used were:

1. By calcination and obtaining the sulphate.

2. By oxidation with mercuric chloride and titrating with standard NaOH.
3. By oxidation with bromine water and precipitating as barium sulphate.
4. By reduction with nascent hydrogen and determining the amount of hydrogen sulphide.

Related Articles

Plessy, *Ann. chim. phys.*, (3) **20,** 162, (1847).

He claimed to have discovered a new series of sulphur acids by the action of sulphur monochloride on sulphurous acid. Salts were prepared from the acids by neutralization with carbonates.

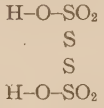
Fordos and Gelis, *Ann. chim. phys.*, (3) **22,** 66, (1848).

They were unable to verify the results of Plessy (*loc. cit.*).

Mendeleeff, *Ber.*, **3,** 870, (1870).
Prin. of Chem. **II,** 284, (1905).

He gives the persulphidic structure to the tetrathionates. Debus, *Jour. Chem. Soc.*, **53,** 351, (1888) states that Mendeleeff adopted the structure of Blomstrand (*Chem. d. Jetzzeit*, 158).

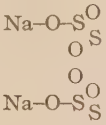
Persulphidic Structure



Gutman, *Ber.*, **37,** 1728, (1905).

He prepared sodium tetrathionate by the method of Fordos and Gelis (*loc. cit.*) and Klobukow (*loc. cit.*). He suggested the peroxidic structure for tetrathionates.

Peroxidic Structure



Gutman, *Ber.*, **39,** 3614, (1907).

He investigated the validity of the results obtained by Fordos and Gelis (*loc. cit.*) and Kessler (*loc. cit.*) on the action of sodium hydroxide on sodium tetrathionate.

Gutman, *Ber.*, **40,** 300, (1908).

An investigation of the action of carbonates of sodium, potassium and lithium on sodium tetrathionate.

Debus, *Jour. Chem. Soc.*, **53,** 278, (1888).
Ann. Chem., **244,** 76, (1888).

He prepared a mixture of potassium thionates by passing sulphur dioxide through a potassium thiosulphate solution.

$$6K_2S_2O_3 + 9SO_2 = K_2S_5O_6 + K_2S_4O_6 + 4K_2S_3O_6$$

Wackenroder's solution was also prepared, the acidity determined, and an equivalent amount of potassium acetate added (assuming pentathionic acid). The solution was evaporated at the ordinary temperature and potassium pentathionate obtained. He further states "The use of potassium acetate instead of potassium hydroxide is advantageous because all the acid of Wackenroder's solution can be converted into the potassium salt, and the hydric acetate which is set free tends to prevent the decomposition of the potassium pentathionate. The mother liquors contain much potassium pentathionate and tetrathionate."

The salt obtained above was analyzed by

(*a*) Oxidation with nitric acid and precipitation with barium chloride.

(*b*) Oxidation with bromine water and precipitation with barium chloride.

The results of the analysis gave results close to the generally accepted ratios of potassium to sulphur, 2:5.

On page 356 a probable structure for tetrathionates is given.

$$\begin{array}{c} K\text{–}S\text{–}SO_2 \\ O \\ S \\ K\text{–}O\text{–}SO_2 \end{array}$$

Chancel and Diacon, *Compt. rend.*, **1,** 710, (1863).
Jour. f. prak. Chem., **90,** 55, (1863).

The tetrathionates of copper and lead were prepared. Tetrathionic acid was also prepared by adding sulphuric acid little at a time to a mixture of lead thiosulphate and lead peroxide.

$$2PbS_2O_3 + PbO_2 + 2SO_3 = PbS_4O_6 + 2PbSO_4$$

Vortmann, *Ber.*, **22,** 2311, (1889).

Arsenic is completely precipitated by sufficient excess of thiosulphate; in presence of arsenious acid there is obtained in the filtrate principally tetrathionic acid besides a trace of pentathionic acid. Sulphuric acid is not formed or only in traces. If too little sodium thiosulphate is present, a part of the arsenious acid remains in solution, and the reaction proceeds according to the equation:

$$As_2O_3 + 9H_2S_2O_3 = As_2S_3 + 3H_2S_4O_6 + 3SO_2 + 6H_2O$$

Two thirds of the sulphur present should go over into the tetrathionate. Two experiments gave 16.08% and 15.46% sulphur instead of 17.14%, calculated from the sodium thiosulphate.

Marshall, *Jour. Soc. Chem. Ind.*, **16,** 396, (1897).

The tetrathionates of potassium and ammonium were prepared by the action of persulphates on thiosulphates.

$$K_2S_2O_8 + 2K_2S_2O_3 = K_2S_4O_6 + 2K_2SO_4$$
$$(NH_4)_2S_2O_8 + 2BaS_2O_3 = (NH_4)_2S_4O_6 + 2BaSO_4$$

Mackenzie and Marshall, *Jour. Chem. Soc.*, II, **93,** 1726, (1908).

Potassium tetrathionate was prepared by the action of potassium persulphate and barium thiosulphate.

$$2BaS_2O_3 + K_2S_2O_8 = K_2S_4O_6 + 2BaSO_4$$

PREPARATION

Sodium tetrathionate was first prepared by following the method given by Biltz and Biltz (Übungbeispeile aus der unorgan. Experimentalchemie, 122): "50 grams of sodium thiosulphate, 26 grams of iodine and 5 grams of water are pulverized in a mortar to a complete homogeneous light brownish yellow paste. In a short time the paste is washed into an Erlenmeyer flask using alcohol as the wash liquid. After about three hours the precipitated sodium tetrathionate is filtered off using suction and washed with alcohol until the filtered alcohol is free of iodine. The crude product is dissolved in 20 grams to 25 grams of lukewarm water, filtered, and alcohol added about 10 grams at a time until about 50 grams have been added. After about ten hours, during which time the mixture has been kept away from the air either in an Erlenmeyer flask or a vacuum desiccator, it is filtered using suction and the crystals washed with alcohol, and dried in a sulphuric acid desiccator. The crystals are colorless and in aggregates. Yield about 20 grams."

The above method is that of Klobukow (*loc. cit.*) somewhat modified; practically the same as given in Biltz, Hall and Blanchard (Laboratory Methods of Inorganic Chemistry, 132); and somewhat similar to that given in Rose-Finkener (*Handb. der analyt. Chem.*, 6 *Aufl.*, **II**, 629).

In following the above directions it was found that the yields were low and variable, being from 20% to 40% of the theoretical.

In order to determine if the yield of the sodium tetrathionate could be increased, a series of experiments were made by precipitating the salt from alcoholic, alcohol-ether, and water solutions and allowing them to stand over night, or to cool them for two or three hours with a mixture of salt and ice.

I—METHOD OF KLOBUKOW (MODIFIED)

The conditions under which the results in Table I, A, B, and C were obtained are as follows:—

50 grams of C. P. $Na_2S_2O_3.5H_2O$ were finely pulverized in a mortar, 5 cc. of alcohol added and then 26 grams of resublimed iodine, which had been previously finely pulverized, were added a little at a time and

thoroughly mixed after each addition. (Whenever the term alcohol is used in this paper, unless otherwise specified, is meant alcohol containing 93% alcohol by weight or about 95% alcohol by volume). The contents of the mortar were transferred to a beaker using alcohol as the wash liquid to completely remove all the residue and then allowed to stand from two to three hours. It was then filtered through a Büchner and washed free of iodine and iodide by means of alcohol and then sucked dry; redissolved in warm water, filtered and reprecipitated as specified in A, B, and C of Table I.

II—METHOD OF SANDER (See D of Table I)

Sodium tetrathionate was prepared according to Sander (*loc. cit.*) except that absolute alcohol-ether (1:1), by volume, at room temperature was used instead of cooled absolute alcohol. The precipitated sodium tetrathionate was redissolved in the smallest amount of warm water, filtered, and added to a mixture of absolute alcohol-ether (1:1) and allowed to stand over night.

TABLE I.

Cc. of water used to dissolve the sodium tetrathionate	Temperature of water °C.	Precipitated from		Cc. used	Yield in %
A. Precipitation by allowing to stand over night.					
25	20	alcohol	=	60	20
18	50	alcohol	=	60	50
18	45	alcohol	=	60	35
17	50	absolute alcohol	=	100	65
17	50	absolute alcohol-ether	=	100	65
B. Precipitation by cooling with a mixture of salt and ice to —10° for three hours.					
19	45	alcohol	=	60	65
14	55	absolute alcohol	=	60	65
16	50	absolute alcohol	=	75	70
14	55	absolute alcohol-ether	=	150	70
C. Precipitation by cooling the saturated water solution to —5° for three hours.					
18	50	water	=	18	40
D. Precipitation according to Sander.					
14	50	absolute alcohol-ether	=	500	60

By reducing the volume of water in which the sodium tetrathionate is redissolved before precipitation, and warming it to increase the solubility and using absolute alcohol or absolute alcohol-ether (1:1) instead of alcohol, the yield was practically doubled. It was found that a fair yield may be obtained from a water solution by cooling with a freezing mixture of salt and ice.

Somewhat better yields were obtained by cooling the solutions rather than by allowing them to stand over night, unless they were placed out of doors when the weather was cold, and under such conditions the yield would sometimes run as high as 80%.

ANALYSIS FOR SULPHUR

In order to get an idea of the purity of the sodium tetrathionate which had been precipitated from a concentrated water solution by the addition of absolute alcohol, a number of experiments were run the results of which are shown in Table II, A, B, and C and in which the sulphur found was compared with the theoretical amount of sulphur, assuming the sodium tetrathionate to be $Na_2S_4O_6 . 2H_2O$.

Procedure:—0.100 gm. to 0.150 gm. of sodium tetrathionate which had been precipitated from alcohol solution and thoroughly dried between filter papers were dissolved in water and bromine water added to distinct bromine coloration.

$$Na_2S_4O_6 + 14Br + 10H_2O = Na_2SO_4 + 3H_2SO_4 + 14HBr$$

The solution was then boiled until the bromine had been driven off and precipitated with barium chloride.

The conditions under which the sulphate ions were precipitated in this series of experiments and all others which follow were: two or three drops of concentrated hydrochloric acid were added to the solution, then heated to boiling and barium chloride solution (made by dissolving 25 gm. of $BaCl_2 . 2H_2O$ in one liter of water) added slowly with constant stirring until about one and one-half times the theoretical amount had been added. The solution was allowed to stand for one-half hour and then filtered through an ashless filter.

The concentration of the sulphate ion before precipitation was kept so that the adsorption by the barium sulphate after precipitation was practically equal to its solubility, *viz.*, about one gram of barium sulphate from a liter of solution.

The Results:—The results of this series of experiments are recorded in

Table II. In trials 1 to 5 inclusive, the sodium tetrathionate solution was contained in a beaker and the bromine water was dropped into it from a pipette, stirring constantly.

In trials 6 to 9 inclusive, the sodium tetrathionate solution was contained in a closed Erlenmeyer flask and the bromine water was added from a drop funnel. In trial 10 the tip of the pipette was placed below the surface of the sodium tetrathionate solution contained in a beaker when the bromine was added, stirring constantly.

TABLE II

	Sodium tetrathionate used Gm.	$BaSO_4$ calc. from sodium tetrathionate taken. Gm.	Sulphur calc. from sodium tetrathionate taken Gm.	$BaSO_4$ found Gm.	Sulphur found Gm.	Error in $BaSO_4$ Gm.	Error in Sulphur Gm.
A. The sodium tetrathionate solution contained in a beaker and the bromine water dropped in from a pipette.							
1.	0.1015	0.3094	0.0425	0.3049	0.0419	−0.0045	−0.0006
2.	0.1016	0.3097	0.0426	0.2999	0.0412	−0.0098	−0.0014
3.	0.1503	0.4582	0.0629	0.4526	0.0622	−0.0056	−0.0007
4.	0.1508	0.4597	0.0632	0.4533	0.0623	−0.0064	−0.0009
5.	0.1515	0.4618	0.0634	0.4569	0.0628	−0.0049	−0.0006
B. The sodium tetrathionate solution contained in a closed flask and the bromine water added from a drop funnel.							
6.	0.1522	0.4639	0.0637	0.4580	0.0629	−0.0059	−0.0008
7.	0.1514	0.4615	0.0634	0.4619	0.0634	+0.0004	0.0000
8.	0.1508	0.4597	0.0632	0.4576	0.0629	−0.0021	−0.0003
9.	0.1506	0.4591	0.0631	0.4573	0.0628	−0.0018	−0.0003
C. The sodium tetrathionate solution contained in a beaker and the bromine water added from a pipette with the tip below the surface of the solution.							
10.	0.1510	0.4603	0.0633	0.4584	0.0630	−0.0019	−0.0003

The results of Table II show that the sodium tetrathionate precipitated by the addition of absolute alcohol is quite pure. Also, in the oxidation of the solution of sodium tetrathionate, certain precautions must be observed in order to prevent loss of sulphur.

QUALITATIVE TESTS

Samples of sodium tetrathionate precipitated from alcohol, alcohol-ether, and water solutions were dissolved in water and tested qualitatively, about 10 cc. of the solution being used for each test.

Solutions added.	Results
Barium chloride	In somewhat concentrated solutions a slight cloudiness was produced.
Lead acetate	None.
Iodine	Small part of a drop gave coloration. N/10 used.
Mercurous nitrate	Yellow precipitate.
Dilute potassium permanganate	Red color. No brown precipitate.
Ferric chloride	Slight coloration in somewhat concentrated solutions.

In dilute solutions the salts dissolved clear, while in more concentrated solutions there was a slight cloudiness. All sodium tetrathionate solutions were neutral to litmus.

For tables showing the characteristic tests for sulphur salts see

Lieb, *Ann.*, **207**, 90, (1881).
Zeitschr. phys. Chem., **47**, 652, (1904).
Prescott and Johnson *Qual., Chem. Anal.*, 7th Ed., 326.

In the above tests the following would be indicated:—Barium chloride in presence of hydrochloric acid would detect presence of sulphates.

Lead acetate would detect presence of iodides.

Iodine would detect the presence of sulphites and thiosulphates.

Mercurous nitrate: dithionates no precipitate; sulphites, thiosulphates, and trithionates a black precipitate; tetrathionates and pentathionates a yellow precipitate.

Dilute potassium permanganate; dithionates and trithionates a red precipitate; tetrathionates and pentathionates bleach.

The qualitative tests show possible traces of free sulphur, and some thiosulphate, the salt crystallized from water solution showing the least.

Pozzi-Escot, *Bul. soc. chim.*, (4), **13**, 401, (1913) gives a very delicate test for thiosulphates, sulphites and polythionates not giving the reaction.

Take 2 cc. of solution containing the thiosulphate and add 2 cc. of a ten per cent ammonium molybdate solution; then add 5 cc. of concentrated sulphuric acid. A blue ring will form between the layers, which may be more readily seen by using a white background. He states .00005 gm. of sodium thiosulphate may be detected.

In order to test the above .0020 gm. of sodium thiosulphate was dissolved in 500 cc. of water and 2 cc. of the solution tested. It gave a blue ring between the layers after about three minutes, using a white background.

COMPARATIVE ANALYSES FOR PURITY

A comparison of the purity of the various samples of sodium tetrathionate was made by determining the amount of sodium sulphate, shown in Table III, A, B, C, and D; and also by determining the total sulphur as barium sulphate, shown in Table IV, A, B, C, and D.

In determining the sodium sulphate it was assumed that the sodium tetrathionate had the composition $Na_2S_4O_6.2H_2O$, and when heated decomposed into sodium sulphate, sulphur dioxide and water.

The results in Table III were obtained by weighing out about one gram of the sodium tetrathionate in a crucible and heating at first with a very low Bunsen flame for a half hour or more keeping the lid on the crucible and gradually raising the heat until the full heat of the Bunsen. Then it was heated with the partial heat of a blast lamp for five minutes, placed in the desiccator, cooled and weighed.

TABLE III

A. Sodium tetrathionate prepared by method of Klobukow, modified, dissolved in water and precipitated by addition of absolute alcohol.

Sodium tetrathionate used. Gm.	Na_2SO_4 calc. Gm.	Na_2SO_4 Found.	Error in Na_2SO_4. Gm.
1.0482	0.4862	0.4883	+0.0021
1.0055	0.4664	0.4682	+0.0018
1.0069	0.4670	0.4694	+0.0024
1.0007	0.4641	0.4668	+0.0027
1.0017	0.4646	0.4667	+0.0021
0.7083	0.3285	0.3306	+0.0021
0.7362	0.3414	0.3435	+.00021

B. Sodium tetrathionate prepared by method of Klobukow modified, dissolved in water and precipitated by the addition of absolute alcohol-ether (1:1).

1.0081	0.4676	0.4716	+0.0040
1.0063	0.4667	0.4700	+0.0033

C. Sodium tetrathionate prepared by the method of Sander dissolved in water and precipitated by the addition of absolute alcohol-ether (1:1).

1.0056	0.4664	0.4760	+0.0096
1.0094	0.4682	0.4778	+0.0096

D. Sodium tetrathionate prepared by method of Klobukow modified, dissolved in water and precipitated from the water solution by cooling with a mixture of salt and ice.

1.0038	0.4656	0.4646	−0.0010
1.0069	0.4670	0.4661	−0.0009

The results given in Table IV were obtained by using the samples of sodium tetrathionate as used to obtain the results in Table III, and in the calculations the same assumption was made as to the composition of the sodium tetrathionate, *viz.*, $Na_2S_4O_6.2H_2O$.

About .1500 gm. of the sodium tetrathionate were weighed, dissolved in water, and bromine water added from a pipette, the tip of which was below the surface of the solution while the bromine water was added, stirring constantly until there was a distinct coloration due to the bromine and then the excess of bromine boiled off.

The same precautions were observed in the precipitation of the barium sulphate as in Table II.

TABLE IV

Sodium tetrathionate used. Gm.	$BaSO_4$ calc. Gm.	Sulphur calc. Gm.	$BaSO_4$ found. Gm.	Sulphur found. Gm.	Error in $BaSO_4$ Gm.	Error in sulphur. Gm.
A. Sodium tetrathionate prepared by the method of Klobukow modified, dissolved in water and precipitated by the addition of absolute alcohol.						
0.1529	0.4661	0.0640	0.4646	0.0638	−0.0015	−0.0002
0.1668	0.5085	0.0699	0.5065	0.0696	−0.0020	−0.0003
B. Sodium tetrathionate prepared by the method of Klobukow modified, dissolved in water, and precipitated by the addition of absolute alcohol-ether (1:1).						
0.1547	0.4716	0.0648	0.4672	0.0642	−0.0044	−0.0006
0.1560	0.4756	0.0653	0.4715	0.0648	−0.0041	−0.0005
C. Sodium tetrathionate prepared by the method of Sander, dissolved in water and precipitated by the addition of absolute alcohol-ether (1:1).						
0.1519	0.4631	0.0636	0.4573	0.0628	−0.0058	−0.0008
0.1510	0.4603	0.0632	0.4544	0.0624	−0.0059	−0.0008
D. Sodium tetrathionate prepared by method of Klobukow modified, and precipitated from the water solution by cooling with a mixture of salt and ice.						
0.1785	0.5441	0.0748	0.5436	0.0747	−0.0005	−0.0001
0.1515	0.4618	0.0635	0.4611	0.0634	−0.0007	−0.0001

The results of the analyses of the various samples of sodium tetrathionate in Tables III and IV show that the salt crystallized from the water solution has the highest degree of purity. However, it might be added that the salt crystallized from the water solution would give a positive test for the presence of thiosulphates by using the ammonium molybdate sulphuric acid test suggested by Pozzi-Escot (*loc. cit.*) if considerable amount of the

sodium tetrathionate be used. The samples of sodium tetrathionate prepared by the method of Klobukow modified, dissolved in water and precipitated by the addition of absolute alcohol or absolute alcohol-ether (1:1), or prepared by the method of Sander and precipitated by the addition of absolute alcohol-ether, always gave a decided test for thiosulphates when the ammonium molybdate sulphuric acid test was applied.

DETERMINATION OF WATER OF CRYSTALLIZATION

Fordos and Gelis (*loc. cit.*) determined the water of crystallization in sodium tetrathionate by difference. Fromm (*loc. cit.*) found it by drying the sodium tetrathionate in the air at 110°.

The water of crystallization was determined in the present investigation by means of a small gas combustion furnace in an atmosphere of carbon dioxide, the arrangement being shown in Fig. 1. The carbon dioxide was obtained from a Kipp generator not shown and passed through a sodium carbonate solution A, and then through two calcium chloride drying columns B. The bottle C and stopcock D were used for convenience. The asbestos shield K protected the absorption tube L from the heat of the furnace. Ordinary copper oxide wire I was used, and the copper spiral H was reduced in the usual way by means of methyl alcohol. The reduced copper spiral H takes up the free sulphur formed from the decomposition of the sodium tetrathionate and decomposes any hydrogen sulphide which may form. During any one combustion only a small part of the reduced copper spiral H next to the boat G was attacked or used by the sulphur. A very small amount of the copper oxide wire was reduced, showing that a very little hydrogen sulphide was formed.

The temperature at which the combustions were carried out was the full heat of the gas combustion furnace in which the glass tube was a bright cherry red.

Before making a determination, the furnace was ignited and the train swept out with carbon dioxide passing at the rate of two bubbles per second until the weight of the calcium chloride absorption tube L was constant to within .4 mg. The time required for this was from three to five hours.

The time required for a determination after placing the sodium tetrathionate in the combustion tube was from three to four hours, which included the gradual heating up of the furnace, the combustion and the sweeping out of the train.

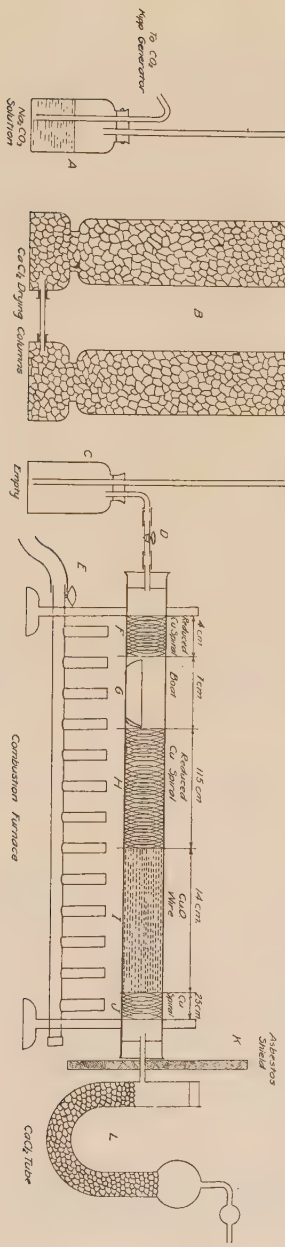

To CO_2 Apparatus
$NaHCO_3$ Solution
A
$CaCl_2$ Drying Columns
B
Empty
C
D
E
4 cm Reduced Cu Spiral
1 cm Boat
11.5 cm Reduced Cu Spiral
14 cm CuO Wire
2.5 cm Cu Spiral
F
G
H
I
J
Combustion Furnace
Asbestos Shield
K
$CaCl_2$ Tube
L

Fig. 1.

The calcium chloride absorption tube L after each combustion was closed on each side and placed in a large sulphuric acid desiccator for one-half hour before each weighing.

Preliminary to the determination of the water of crystallization in the sodium tetrathionate, two combustions were made with some selected crystals of C. P. sodium thiosulphate, the results being shown in Table V, A. The sodium tetrathionate used in the experiments shown in Table V, B, was crystallized from a water solution by cooling with salt and ice and dried between filter papers.

TABLE V

A. Determination of water of crystallization in hydrous sodium thiosulphate.

Weight of sodium thiosulphate taken. Gm.	Weight of sodium tetrathionate taken. Gm.	Weight of water found. Gm.	Weight of water calc. Gm.	Error in Gm.
0.3841	.....	0.1391	0.1394	−0.0003
0.4852	.....	0.1753	0.1761	—0.0008

B. Determination of water of crystallization in hydrous sodium tetrathionate.

.....	1.1998	0.1414	0.1411	+0.0003
.....	1.1914	0.1407	0.1401	+0.0006

In making the calculations for the water of crystallization in hydrous sodium thiosulphate and hydrous sodium tetrathionate in A and B of Table V, their compositions were assumed to be $Na_2S_2O_3.5H_2O$ and $Na_2S_4O_6.2H_2O$ respectively.

The results in B of Table V show that each molecule of hydrous sodium tetrathionate contains two molecules of water of crystallization.

BEHAVIOR WHEN EXPOSED TO AIR AT ORDINARY ATMOSPHERIC PRESSURES; TO AIR OVER SULPHURIC ACID AT ORDINARY AND REDUCED ATMOSPHERIC PRESSURES

Klobukow (*loc. cit.*), Biltz and Biltz (*loc. cit.*) and Sander (*loc. cit.*) in the preparation of sodium tetrathionate direct to dry the salt over sulphuric acid. Sander (*loc. cit.*) stated that he was unable to prepare pure hydrous sodium tetrathionate, yet he prepared pure anhydrous potassium tetrathionate using the same method, drying both salts over sulphuric acid.

In order to determine the behavior of hydrous sodium tetrathionate when exposed to the air at ordinary atmospheric pressure, to air over

sulphuric acid at ordinary and also reduced atmospheric pressures, the experiments the results of which are shown in Table VI, A, B, and C were made. The sodium tetrathionate was spread out on one of two tared watch glasses.

TABLE VI

A. Hydrous sodium tetrathionate exposed to air.

Weight of sodium tetrathionate Gm.	Time exposed. Days.	Loss in weight of sodium tetrathionate. Gm.
1.0040	0	0.0000
1.0045	2	+0.0005
1.0044	10	+0.0004

B. Hydrous sodium tetrathionate exposed to air over concentrated sulphuric acid at ordinary atmospheric pressure.

1.0042	0	0.0000
1.0035	1	0.0007
1.0032	2	0.0010
1.0016	4	0.0026
1.0011	5	0.0031
1.0010	6	0.0032
0.9998	8	0.0044
0.9982	11	0.0060

C. Hydrous sodium tetrathionate exposed to air over concentrated sulphuric acid at reduced atmospheric pressure (from two to five cm. of Hg).

0.9982	0	0.0000
0.9970	2	0.0012
0.9960	3	0.0022
0.9789	15	0.0193
0.9647	27	0.0335

The results obtained in Table VI, A, show that the weight of hydrous sodium tetrathionate is fairly constant in the air, the slight changes shown being due to decided changes in the humidity; those in B and C show a gradual loss in weight over sulphuric acid, either at ordinary or reduced atmospheric pressure. Further, the results show that the dissociation pressure of hydrous sodium tetrathionate is of such magnitude that it should not be dried over concentrated sulphuric acid for any considerable length of time.

SUGGESTED METHOD FOR PREPARATION

Weigh out 50 grams of $Na_2S_2O_3.5H_2O$ and 26 grams of iodine and pul-

verize each in separate mortars. To the finely pulverized sodium thiosulphate in the mortar, add approximately 5 cc. of distilled water and 25 cc. of alcohol and thoroughly mix. Then add the iodine a little at a time, thoroughly mixing after each addition, until all has been added and there remains a slight excess of iodine. Add 25 cc. of alcohol and allow to stand from twenty minutes to one half hour, filter through a Büchner using suction, and wash free of iodine and iodide by means of alcohol.

The absence of iodine may be told by the color of the wash alcohol, and the absence of iodide by the addition of a few drops of a dilute solution of lead acetate to the wash alcohol. Lead acetate when added to the wash alcohol forms a yellow precipitate of lead iodide when an iodide is present, and a white precipitate of lead tetrathionate when it is absent.

The precipitate after it has been sufficiently washed with alcohol is sucked nearly dry on the Büchner in order to remove most of the alcohol, dissolved in the smallest possible amount of water (15 cc. to 17 cc.), warmed to 50° to 60° and filtered through a Gooch using suction into a test tube which is placed within a one liter Erlenmeyer filter flask. To this filtrate add ten to fifteen drops, or if necessary more, of iodine in alcohol solution. There should be a slight iodine coloration.

The sodium tetrathionate may be precipitated or crystallized from the filtrate by the addition of absolute alcohol-ether (1:1) or absolute alcohol and allowing to stand over night, or by cooling with a mixture of salt and ice.

(I) *Precipitation by the addition of absolute alcohol-ether or absolute alcohol and allowing to stand over night.*

Add the filtrate to a crystallizing dish and then add 100 cc. of absolute alcohol-ether (1:1) and place in an empty desiccator (best a vacuum desiccator) for at least twelve hours.

Instead of using absolute alcohol-ether (1:1), 100 cc. of absolute alcohol may be used with nearly the same yield.

(II) *Precipitation by the addition of absolute alcohol-ether or absolute alcohol and cooling by means of salt and ice.*

Add the filtrate to a small beaker and then add 100 cc. of absolute alcohol-ether (1:1) and cool by placing in a mixture of salt and ice for two or three hours, keeping the beaker covered. Absolute alcohol may be substituted for the absolute alcohol-ether as in (I).

Whether the sodium tetrathionate is precipitated by (I) or (II), it

should be filtered using suction and sucked as dry as possible, then placed between filters and dried. It should then be crystallized from a water solution by cooling as this removes practically all the thiosulphate.

Recrystallization from Water. The dry sodium tetrathionate obtained from the absolute alcohol-ether or the absolute alcohol mixtures is dissolved in the smallest amount of water at 50° to 60° in a beaker and cooled by a mixture of salt and ice for two or three hours. This will give about one half of the sodium tetrathionate dissolved. The sodium tetrathionate precipitated should be filtered off using suction to remove the greater part of the water, then placed between filter papers until dry. After the salt has been dried, it should be placed in a glass stoppered bottle.

In case it is desired, the greater part of the sodium tetrathionate still dissolved in the mother liquor or filtrate may be precipitated by the addition of absolute alcohol-ether (1:1) or absolute alcohol.

Stability of Sodium Tetrathionate. Two different samples of sodium tetrathionate crystallized from water and thoroughly dried between filter paper were kept in glass stoppered bottles for one and one-half years. One sample had a very slight tinge of yellow and when dissolved in water showed some turbidity; the other sample remained perfectly white and when dissolved in water showed only the slightest trace of turbidity.

Sander (*loc. cit.*) says that solutions of pure tetrathionates may be boiled without decomposition. He further states that the presence of sodium thiosulphate greatly accelerates the decomposition.

BARIUM TETRATHIONATE

BIBLIOGRAPHY

Fordos and Gelis, *Ann. chim. phys.*, (3) **6**, 489(1842).

Jour. f. prak. Chem., **28**, 476(1843).

Barium tetrathionate was prepared by the action of iodine on barium thiosulphate.

Barium thiosulphate was mixed with water forming a thin paste and small amounts of iodine were added until it just began to color; the excess of iodine and iodide were washed out with alcohol. The white powder was dissolved in the smallest amount of water possible, filtered and allowed to evaporate. The crystals were more readily obtained when absolute alcohol was added to the solution.

The barium tetrathionate had a bitter taste, was very soluble in water, slightly in alcohol, kept at the ordinary temperature in dry air but became yellow in a short time in moist air.

They made an analysis of the salt as follows:—A known amount of the salt was dissolved in water and oxidized with chlorine. The solution was filtered, and the barium sulphate formed was weighed. The sulphuric acid formed during the oxidation was precipitated with barium chloride.

The water of crystallization was found by difference.

Wackenroder, *Archiv. der Pharm.*, **47,** 272, (1846).

Wackenroder's solution was prepared by passing hydrogen sulphide into a saturated water solution of sulphur dioxide at room temperature until there was an excess of hydrogen sulphide. The solution was then shaken with some oxidized copper turnings and filtered. This filtrate was immediately completely neutralized with barium carbonate and a little barium hydroxide, and after a few hours the solution was ready to be used.

(*a*) A known weight of the barium pentathionate solution was taken and the barium determined by precipitation with sulphuric acid.

(*b*) A known weight of the barium pentathionate solution was taken and a solution of potassium hydroxide added and the solution evaporated to dryness. The residue was dissolved in water, nitric acid added, and the solution boiled. This solution was evaporated to dryness, the residue dissolved in water and a solution of barium chloride added. The results of the first trial showed the ratio of the barium to the sulphur to be 1:5.23. In the second trial the ratio of barium to sulphur was found to be 1:5.

Wackenroder, *Archiv. of Pharm.*, **48,** 140, (1846).

This was a continuation of the previous article and the results are no more satisfactory. The water of crystallization was determined by heating the barium salt to 105° C.

Lenoir, *Ann. Chem. u. Pharm.*, **62,** 253, (1847).

Barium pentathionate was prepared by treating Wackenroder's solution with barium carbonate, the salt being precipitated by the addition of alcohol. On analysis the salt was found to have practically the composition, $BaS_5O_6 . 2H_2O$.

The water of crystallization was determined by combustion with lead chromate; at the same time carbon dioxide was determined and the carbon corresponded to 2.93% alcohol which was present in the salt.

Ludwig, *Archiv. der Pharm.*, **51,** 259, (1847).

Potassium tetrathionate was prepared from Wackenroder's solution by half neutralizing with potassium carbonate. Barium and lead salts were prepared in a similar way.

Kessler, *Jour. f. prak. Chem.*, **47,** 35, (1849).
Pogg. Ann. Phys. Chem., **74,** 255, (1849).

Barium tetrathionate was prepared by using equivalent amounts of solutions barium acetate and tetrathionic acid and then adding alcohol. The crystals were tabular. The analysis of the salt was not given.

Sobrero and Selmi, *Ann. chim. phys.*, (3) **28,** 210, (1850).

Barium tetrathionate was prepared from Wackenroder's solution by the addition of barium carbonate. On analysis the results obtained for baryte, sulphur, oxygen combined with sulphur and water agree very favorably with those of Fordos and Gelis (*loc. cit.*).

Spring, *Ann. Chem. Pharm.*, **199,** 97, (1879).

The potassium and barium tetrathionates were prepared from Wackenroder's solution by neutralizing with the carbonates and then adding alcohol. The salts showed on analysis, K:S = 2:4 and Ba:S = 1:4.

Pfeiffer, *Arch. Pharm.*, **14,** 334, (1879).

Potassium tetrathionate was prepared from Wackenroder's solution which had been brought to a specific gravity of 1.30 by evaporation on a water bath. This acid was dissolved in a mixture of ether-amyl alcohol and absolute alcohol and a dilute solution of potassium carbonate added. The barium salt was prepared in a similar way except it was precipitated from alcohol.

The salts were analyzed in two ways.

(*a*) By oxidation with bromine in hydrochloric acid solution and precipitation with barium chloride.

(*b*) By heating and determining the sulphates.

He concluded from his results that pentathionic acid does not exist free nor in the form of salts.

Smith and Takamatsu, *Jour. Chem. Soc.* **37,** 592, (1880).

Barium tetrathionate was prepared from Wackenroder's solution by neutralizing with barium carbonate and precipitating with alcohol. The salt on analysis proved to be $BaS_4O_6 . 1\ H_2O$. They further state, "We have proved to our own satisfaction that the attempt to neutralize pentathionic acid with alkaline earth carbonates simply results in the formation of tetrathionates with the separation of sulphur."

Lewes, *Jour. Chem. Soc.* **39,** 68, (1881).

The pentathionates and tetrathionates of potassium and barium were prepared.

Wackenroder's solution was concentrated to the separation of sulphur and filtered. The acidity was then determined by titration with standard potassium hydroxide, then a weak solution of barium hydroxide sufficient to half neutralize the acid was added; the next day it was filtered to remove the sulphur and barium sulphate which formed. The filtrate was then placed over sulphuric acid in a vacuum and left to crystallize. After standing a few days some sulphur separated and the solution was again refiltered and replaced in the vacuum over sulphuric acid. At the end of eighteen days it deposited a crop of fine needle shaped crystals together with a small quantity of sulphur. Three crops of crystals were obtained, and each crop was then dissolved in a small amount of water and recrystallized a second time. The first crop showed on analysis to be $BaS_4O_6 . 3H_2O$; the second seemed to be a mixture of the pentathionate and the tetrathionate; the third seemed to have the composition $BaS_5O_6 . 3H_2O$.

The methods he used in the analysis were,

(*a*) Oxidation with nitric acid, removal of all traces of acid, filtering and weighing the barium sulphate. The rest of the sulphur being oxidized to sulphuric acid was precipitated as barium sulphate.

(*b*) Oxidation with chlorine in potassium hydroxide solution.

(*c*) Boiling the solution with mercuric cyanide and estimation of sulphuric acid, mercuric sulphide and free sulphur, according to the equation of Kessler, (*loc. cit.*).

(*d*) Evaporation of solution to dryness with potassium hydroxide and fuse with potassium hydroxide and potassium nitrate, precipitating as barium sulphate.

The water of crystallization was determined by combustion with lead chromate.

Spring, *Ann. Chem.*, **213,** 329, (1882).

The potassium and barium salts were prepared from Wackenroder's solution by neutralizing with carbonates and precipitating with alcohol. He also treated potassium thiosulphate with sulphur monochloride and obtained a salt which showed on analysis K:S 2:4.02.

He has compiled a list of the results of the different investigators who have prepared potassium pentathionate from Wackenroder's solution. The ratio of potassium to sulphur varies from 2:3.305 to 2:5.23, the average being 2:4.506.

Spring held that what is called pentathionic acid is nothing but sulphur dissolved in tetrathionic acid.

Smith and Takamatsu, *Jour. Chem. Soc.*, **41,** 162, (1882).

Potassium and barium salts were prepared in a similar way to that already used in their previous article (*loc. cit.*).

Curtius and Henkel, *Jour. f. prak. Chem.*, N. F. **37,** 142, (1888).

Barium tetrathionate was prepared from Wackenroder's solution and barium carbonate.

The Wackenroder's solution was filtered and placed in a large flask and barium carbonate added a little at a time until an excess had been added. It was kept in the flask for several hours during which time it was thoroughly shaken; the solution was then filtered, the filtrate being clear and did not react with litmus. A portion of the filtrate was analyzed and the ratio of Ba to S was found to be 1:4.

The salt was obtained by filtering any excess barium carbonate and adding alcohol. The barium tetrathionate thus obtained was dissolved in a small amount of water and reprecipitated by alcohol. The salt obtained from the second precipitation was analyzed and found to have the composition $BaS_4O_6.2H_2O$.

The Analysis:—a known amount of the salt was dissolved in water and then oxidized with chlorine in potassium hydroxide solution. The solution was then filtered and the barium sulphate weighed. The sulphuric acid formed during the oxidation was precipitated by the addition of barium chloride and weighed as barium sulphate.

The water of crystallization was determined by combustion with lead chromate.

Hertlein, *Zeitschr. f. phys. Chem.*, **19,** 287, (1896).

Potassium Tetrathionate:—To a completely saturated solution of potassium thio-

sulphate at room temperature, so arranged as to be cooled and constantly stirred, was a water solution of iodine in potassium iodide added dropwise, and after each addition of iodine waited until it had been decolorized. The crystallized potassium tetrathionate was filtered off from time to time to avoid the action of iodine on the tetrathionate.

Barium Tetrathionate:—It was prepared by making a paste with barium thiosulphate and water and adding solid iodine in small amounts at a time until a distinct brown color remained. The salt was then washed with strong alcohol and the excess of iodine and iodide removed, dissolved in water and a small amount of alcohol added which precipitated a small amount of barium tetrathionate and which was of particular aid in removing the finely divided sulphur and barium sulphate. The solution was then filtered and the rest of the barium tetrathionate precipitated by the further addition of alcohol.

The concentrated solutions of the barium salt decompose slightly and on this account it was impossible to get it perfectly clear. The salt dissolves with residue but the solutions are always more or less opalescent; solutions of moderate concentration do not show this.

PREPARATION

I. *Previous Methods Used.*

Barium tetrathionate was first prepared by Fordos and Gelis (*loc. cit.*). Since that time many investigators have prepared the salt, their methods being as follows:—

(1) By action of iodine on barium thiosulphate. Fordos and Gelis (*loc. cit.*); Hertlein (*loc. cit*).

(2) From Wackenroder's solution.

(*a*) By half neutralizlng with potassium carbonate. Ludwig (*loc. cit.*).

(*b*) By half neutralizlng with barium hydroxide. Lewes (*loc. cit.*).

(*c*) By complete neutralization with barium carbonate. Sobrero and Selmi (*loc. cit.*); Spring (*loc. cit.*); Pfeiffer (*loc. cit.*); Smith and Takamatsu (*loc. cit.*); Curtius and Henkel (*loc. cit.*).

(3) By action of barium acetate on tetrathionic acid. Kessler (*loc. cit.*).

II. *General Procedure of Method Used.*

25 grams of $BaS_2O_8.1H_2O$ and 12.5 grams of resublimed iodine were finely pulverized in separate mortars. Then from 80 to 100 cc. of alcohol of definite density were added to the mortar containing the barium thiosulphate and the iodine added a little at a time thoroughly mixing after each addition, until all the iodine had been added and there remained a slight excess of iodine.

The mixture was left in the mortar from two to three hours stirring occasionally, transferred to a Büchner using alcohol as the wash liquid and washed free of iodine and iodide by means of alcohol.

The residue was dissolved in the smallest possible amount of water at a temperature not above 20°, filtered through a specially prepared Gooch and the barium tetrathionate precipitated from the filtrate by the addition of alcohol, absolute alcohol, absolute alcohol-ether (1:1), or acetone either by allowing to stand over night or by cooling, the results being shown in A, C, and D of Table VII. In B of Table VII is shown the result obtained by cooling the water solution of barium tetrathionate.

III. *Preparation of Barium Thiosulphate.*

The barium thiosulphate was prepared by mixing solutions containing equivalent amounts of sodium thiosulphate and barium chloride.

463.9 grams of C. P. hydrous sodium thiosulphate were dissolved in 550 cc. of water, and 456.6 grams of C. P. hydrous barium chloride were dissolved in 1500 cc. of water, both solutions being filtered before used.

The solution of sodium thiosulphate was heated nearly to boiling and kept hot while the barium chloride solution was added from a burette at the rate of two or three drops per second, stirring constantly.

After all the barium chloride had been added, the barium thiosulphate was washed by decantation six or eight times, then placed on a Buchner and washed, using suction until free of chlorides.

IV. *Difficulties Encountered.*

In the first experiments in which barium tetrathionate was prepared several difficulties were encountered and the yields were very low.

(1) Barium thiosulphate does not form paste.

The barium thiosulphate did not form a paste with water as did the sodium thiosulphate and for this reason the condition for complete reaction was not so good.

(2) Reaction incomplete.

When alcohol alone was added to the barium thiosulphate and the iodine added a little at a time, the reaction would not go to completion and a large residue of barium thiosulphate remained. These results are shown in Table VII, trials 1 to 8 inclusive. This difficulty was probably of a mechanical nature due to a protective coating of barium tetrathionate formed around the particles of barium thiosulphate thus preventing the contact with the iodine in solution. When water was added to the alcohol

which was added to the barium thiosulphate before the addition of the iodine, the reaction would go to completion. The addition of water to the alcohol either increased the solubility of the barium tetrathionate and thus removed the protective coating, or permitted the barium tetrathionate to be formed in a more granular form and the protective coating did not form; in either case the reaction would go to completion.

(3) Determination of density of alcohol used.

Since it was shown that water must be added to the alcohol which was added to the barium thiosulphate before the addition of iodine, it was necessary to determine the density of alcohol used which would permit the reaction to go to completion and still not have the water content high enough to dissolve any considerable amounts of barium tetrathionate. This was done by increasing the density of the alcohol used until there was no residue of barium thiosulphate.

(4) The condition of the barium tetrathionate formed.

The barium tetrathionate, obtained when undiluted alcohol was added to the barium thiosulphate before the addition of iodine, was gummy and difficult to filter; while the barium tetrathionate, obtained when diluted alcohol was used, was crystalline and easily filtered.

TABLE VII

A. Precipitated by allowing to stand over night. Alcohol specific gravity 0.817 at 20°, added to the barium thiosulphate.

Trial.	Cc. of alcohol added to barium thiosulphate	Cc. of water used to dissolve barium tetrathionate.	Precipitated from.		Cc. used.	Yield in %.
1	350	14	alcohol	=	60	8
2	3 cc. water 20 cc. alcohol	14	ab. alcohol	=	60	21.5
3	20	35	ab. alcohol	=	100	12.1
4	40	26	ab. alcohol	=	100	10.7
5	35	20	ab. alcohol	=	200	13.7
6	50	20	ab. alc.-ether	=	200	26.9
7	50	20	acetone	=	170	10.2

B. Precipitated by cooling a water solution. Alcohol specific gravity 0.817 at 20° added to the barium thiosulphate.

8	50	23	water	=	23	9.1

C. Precipitated from an absolute alcohol-ether solution (1:1) by cooling. Alcohol specific gravity 0.887 at 20° added to barium thiosulphate.

9	85	25	abs. alc.-ether	=	200	40.3

D. Precipitated by allowing to stand over night. Alcohol specific gravity 0.887 at 20° added to barium thiosulphate.

10	90	35	abs. alc.-ether =	250	59.
11	90	36	abs. alc.-ether =	400	70.
12	110	27	abs. alc.-ether =	400	65.
13	100	30	abs. alc.-ether =	500	70.

The results of the above experiments show that the highest yields were obtained when absolute alcohol-ether was added to the filtrate and allowed to stand over night. The low results in the first eight trials was largely due to the fact that the reaction between the iodine and barium thiosulphate did not go to completion.

COMPARATIVE ANALYSIS FOR PURITY

I. *By Heating the Barium Tetrathionate.*

In order to get an idea of the purity of the barium tetrathionate a series of experiments were made, the results of which are shown in Tables VIII and IX.

TABLE VIII

A. Barium tetrathionate prepared by the method of Fordos and Gelis modified, dissolved in water and precipitated by the addition of absolute alcohol-ether (1:1).

Trial.	Barium tetrathionate used. Gm.	Barium sulphate calculated. Gm.	Barium sulphate found. Gm.	Error in barium sulphate. Gm.
1	0.5025	0.2950	0.2968	+0.0018
2	0.5048	0.2963	0.2979	+0.0016
3	0.5002	0.2936	0.2948	+0.0013
4	0.5031	0.2953	0.2981	+0.0028
5	0.4955	0.2908	0.2887	−0.0021
6	0.5060	0.2970	0.2954	−0.0016
7	0.5047	0.2952	0.2943	−0.0019
8	0.5020	0.2947	0.2923	−0.0024
9	0.5099	0.2993	0.2994	+0.0001
10	0.4983	0.2925	0.2927	+0.0002
11	0.5180	0.3041	0.3055	+0.0014
12	0.5046	0.2962	0.3008	+0.0046
13	0.5023	0.2949	0.2974	+0.0025
14	0.5007	0.2939	0.2961	+0.0022

B. Barium tetrathionate prepared by the method of Fordos and Gelis modified, dissolved in water and cooled.

15	0.5139	0.3017	0.3014	−0.0003
16	0.5014	0.2943	0.2942	−0.0001

In Table VIII are shown results obtained by heating the barium tetrathionate.

About one half gram of the hydrous barium tetrathionate was weighed out into a crucible and heated with a very low Bunsen flame for about one-half hour, keeping the lid loosely fitted on the crucible, then gradually raising the temperature to the full heat of the Bunsen for ten minutes, placed in a desiccator, cooled and weighed. In some cases a few drops of concentrated sulphuric acid were added to the barium sulphate and then carefully driven off by heating; this made no change in the results.

In calculating the barium sulphate from the hydrous barium tetrathionate, the composition of the hydrous barium tetrathionate was assumed to be $BaS_4O_6.2H_2O$, and the products formed when heated to be barium sulphate, sulphur dioxide and sulphur.

II. *By Oxidation of Barium Tetrathionate and Precipitating with Barium Chloride Solution*

The results shown in Table IX were obtained by weighing out given amounts of hydrous barium tetrathionate, dissolving in water, oxidizing with bromine water and afterwards boiling off the excess, and precipitating the sulphate ion by the addition of a barium chloride solution observing all the precautions given under Table II.

The hydrous barium tetrathionate was obtained by addition of an absolute alcohol-ether (1:1) solution to a freshly filtered concentrated water solution of barium tetrathionate and allowing to stand over night.

TABLE IX

Barium tetrathionate taken. Gm.	Barium sulphate calculated. Gm.	Barium sulphate found. Gm.	Error in barium sulphate. Gm.
1.0000	2.3480	2.2976	−0.0514
0.5000	1.1740	1.1604	−0.0136
0.5000	1.1740	1.1587	−0.0153

The results shown in Table VIII, trials 1 to 4 inclusive were obtained from two different samples, but the samples were analyzed about three weeks after they were prepared; the results in trials 5 to 8 inclusive were obtained from two other different samples analyzed two days after their preparation; the results in trials 9 to 14 were from three entirely different samples analyzed two days after their preparation.

The results in B, Table VIII, were obtained from a sample precipitated

from a water solution, carefully dried between filters and immediately analyzed.

It might also be stated that the results obtained in trials 9 to 14 inclusive were from samples prepared during the hot summer months.

The results of both Tables VIII and IX show the hydrous barium tetrathionate to be quite pure, but it slowly decomposes particularly above 20°.

WATER OF CRYSTALLIZATION

Fordes and Gelis (*loc. cit.*) obtained the salt from a water solution and found that each molecule of the salt contained two molecules of water of crystallization, the result being obtained by difference. Sobrero and Selmi (*loc. cit.*) obtained results in agreement with those of Fordos and Gelis. Lewes (*loc. cit.*) obtained two salts of hydrous barium tetrathionate, one of which contained one and the other three molecules of water of crystallization. The results were obtained by combustion with lead chromate. Curtius and Henkel (*loc. cit.*) determined the water of crystallization by combustion with lead chromate and found it to contain two molecules of water of crystallization. Hertlein (*loc. cit.*) prepared barium tetrathionate according to the method of Fordos and Gelis, precipitated by means of alcohol and dried the salt over sulphuric acid and found that it contained one molecule of water of crystallization. He does not state the results of his analysis nor does he state what method he used.

BEHAVIOR OF THE HYDROUS SALT WHEN EXPOSED TO AIR; TO AIR OVER CONCENTRATED SULPHURIC ACID AND TO AIR SATURATED WITH MOISTURE

In order to determine the behavior of hydrous barium tetrathionate when exposed to air, air over concentrated sulphuric acid, and air saturated with moisture, a series of experiments were carried out, the results of which are shown in Table X.

The hydrous barium tetrathionate was spread out on one of two tared watch glasses. In A, the watch glasses were exposed to air; in B, to air over concentrated sulphuric acid in a desiccator; in C, to air over water in a desiccator.

The results of Table X seem to show that hydrous barium tetrathionate is slightly deliquescent when exposed to air. Further, that when exposed

to air over concentrated sulphuric acid it slowly loses some of its water of crystallization.

TABLE X

Weight of hydrous barium tetrathionate. Gm.	Time exposed. Days.	Loss in weight. Gm.	Gain in weight. Gm.
A. Hydrous barium tetrathionate exposed to air.			
1.0058	0	.....	0.0000
1.0058	2	.....	0.0000
1.0075	10	.....	0.0017
B. Hydrous barium tetrathionate exposed to air over concentrated sulphuric acid.			
1.0075	0	0.0000	.....
1.0040	2	0.0035	.....
0.9977	8	0.0098	.....
0.9927	14	0.0148	.....
0.9918	20	0.0157	.....
C. Exposed to saturated air.			
1.0052	0	.....	0.0000
1.2905	2	.....	0.2853

SUGGESTED METHOD FOR PREPARATION

Weigh out 50 grams of $BaS_2O_3.1H_2O$ and 25 grams of iodine, placing each in separate mortars and pulverize them very fine. To the barium thiosulphate in the mortar add 100 cc. of alcohol specific gravity approximately 0.887 at 20° and thoroughly mix. Then add the iodine a little at a time, mixing thoroughly after each addition, until all the iodine has been added and there remains a slight excess of iodine. The addition and mixing should require about three quarters of an hour. Allow the mixture to remaln in the mortar a short time after all the iodine has been added and filter through a Buchner using suction.

Wash the precipitate free of iodine and iodide by use of alcohol. The absence of iodine may be told by the color of the wash alcohol; the absence of iodide by the addition of a few drops of a dilute solution of lead acetate.

After these impurities have been removed, the precipitate is dried as much as possible by pressing between filter paper to remove most of the alcohol. This nearly dry precipitate is then dissolved in the least possible amount of water (about 65 cc.) at not above 20°. This solution is then filtered using suction through a specially prepared Gooch, which consists of two separate layers of barium sulphate and flowers of sulphur with a

layer of asbestos on the top and bottom and also between each of the four layers. This solution is best filtered into a test tube placed within an Erlenmeyer filtering flask. To the filtrate add several drops of iodine dissolved in alcohol to a slight iodine coloration. This filtrate, which usually has a slight turbidity, is added to 700 cc. of absolute alcohol-ether (1:1) in a crystallizing dish, placed in an empty vacuum desiccator and the air removed and allowed to stand from twelve to twenty-four hours. If the weather is cold the yield is increased by placing out of doors. The yield is 60% to 75% of the theoretical.

Recrystallization from a water solution.

Hydrous barium tetrathionate may also be obtained by cooling the water solution by means of a mixture of salt and ice. The rate of crystallization is extremely slow and the yield not very satisfactory.

QUALITATIVE DECOMPOSITION

The salts of the tetrathionate decompose into a sulphate, sulphur dioxide, and sulphur when heated. In order to get an idea of the decomposition of tetrathionates in a boiling solution, a series of qualitative experiments were made.

About 1 gram of hydrous barium tetrathionate was dissolved in 100 cc. of water and transferred to an Erlenmeyer flask which was attached to a Liebig condenser. The solution was heated and became decidedly turbid as soon as it began to boil.

The odor of sulphur dioxide was plainly noticeable at the mouth of the condenser, and when the evolved gas was led into a dilute solution of potassium permanganate it was readily bleached.

The residue consisted of barium sulphate and sulphur with a slight trace of sulphite and thiosulphate.

The solution was boiled for 30 hours and when tested with mercurous nitrate solution gave a yellow precipitate indicating the presence of tetrathionate or pentathionate or both, or possibly higher thionates, but the absence of any appreciable amounts of trithionate, sulphite, or thiosulphate. Further, tests were made to determine if any hydrogen sulphide were formed during the decomposition.

(I) Filter paper moistened with lead acetate solution was held at the mouth of the condenser and negative results obtained.

(II) Several drops of lead acetate solution were added to the solution

of barium tetrathionate and the solution boiled with a reflux for one hour before any darkening was noticeable. At the end of two hours the solution began to turn black, and at the end of six hours it was black.

The results of the above qualitative tests show that the barium tetrathionate solution when boiled decomposes into barium sulphate, sulphur dioxide, and sulphur.

QUANTITATIVE DECOMPOSITION

(I) *Preliminary.*

Before making the quantitative determinations some preliminary experiments were made to get some idea of the time required for the decomposition.

1. 1 gram of hydrous barium tetrathionate was dissolved in water and placed in a flask attached to a reflux condenser and boiled 8.5 hours. The solution was filtered and again boiled 2 hours. The weight of barium sulphate obtained by the second boiling was .0143 grams.

2. 1 gram of hydrous barium tetrathionate was treated exactly as in 1 except it was boiled the first time for 8 hours. The solution was filtered and again boiled for 5.5 hours. The weight of barium sulphate obtained by the second boiling was .0179 grams.

3. 1 gram of hydrous barium tetrathionate was treated as in 1 except it was boiled for 7.5 hours. The weight of barium sulphate obtained was .4160 grams as compared to .5870 grams, the theoretical yield.

(II) *Description of the Apparatus.*

After considerable experimenting the set-up shown in Fig. 2 was chosen, although in carrying out the experiments two absorption tubes in series were used.

The carbon dioxide was generated by a Kipp not shown and then passed through a solution of sodium carbonate contained in A to the decomposition flask C, the inlet tube extending below the surface of the solution. The decomposition flask C was attached to a reflux condenser B in order to prevent loss by boiling and thus keep the volume of the solution constant. Connected to the reflux condenser B was a ten bulbed Meyer absorption tube D which contained the bromine water or alkaline hypobromite to oxidize the evolved sulphur dioxide. E was filled with some of the same solution as was used in the absorption tube.

The type of absorption tube used was the same as used by Lunge, *Jour. Soc. Chem. Ind.*, **9**, 1013 (1890).

(III) *Procedure.*

The apparatus was first tested to be sure there were no leaks. After the set-up was found to be gas tight, 1.0000 gram of hydrous barium tetrathionate was dissolved in water and transferred quantitatively to the decomposition flask C so there were 100 cc. of solution in the flask. The air in the system was then driven out by the carbon dioxide and the solu-

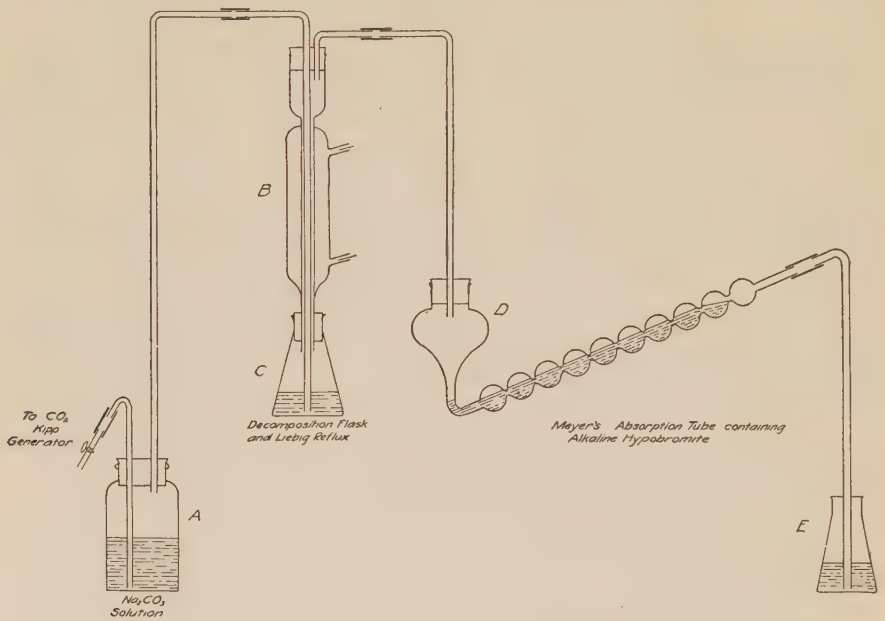


Fig. 2.—Decomposition and Absorption Apparatus.

tion heated. After the boiling had started the carbon dioxide was continued at the rate of about two bubbles per second during the entire time of the boiling. When the boiling was discontinued, the system was swept out by carbon dioxide for one half hour.

The analysis shown in Table XI consists of three parts.

(1) Determination of barium sulphate obtained from the direct decomposition of the barium tetrathionate during the boiling.

The contents of the decomposition flask was transferred quantitatively to a beaker, together with the small amount of sulphur which collected in the lower part of the condenser. The solution was then filtered through a hard filter and the filter thoroughly washed with water. The residue on the filter, which consisted of barium sulphate and sulphur, was washed into a beaker and liquid bromine added, the solution being kept warm for three hours. The decomposition flask was also treated with hot bromine water to remove any adhering particles of sulphur, and this solution added to that containing the barium sulphate and sulphur.

The free sulphur was oxidized to sulphuric acid, while the barium sulphate remained unchanged.

The solution was then boiled to remove the bromine and filtered through a weighed Gooch, the increase in weight being the barium sulphate formed from the direct decomposition of the barium tetrathionate.

(2) Determination of barium sulphate obtained from the sulphur formed during the boiling.

The filtrate obtained from (1) should contain all the sulphur formed during the decomposition by boiling as sulphuric acid. The sulphate ion was precipitated by the addition of a solution of barium chloride, the barium sulphate being that obtained from the oxidation of the sulphur.

(3) Determination of barium sulphate obtained from the sulphur dioxide formed during the boiling.

When bromine was used in the absorption tubes as in trials 1 to 12 inclusive, the contents of the tubes was transferred quantitatively to a beaker, the excess bromine boiled off, and precipitated by the addition of a solution of barium chloride.

When alkaline hypobromite was used in the absorption tubes as in trials 13, 14 and 15 the contents of the tubes was transferred quantitatively to a beaker, made slightly acid with hydrochloric acid and carefully evaporated to dryness, the last stages being on a water bath. The beaker containing the residue was then heated in an air oven at 120° for two hours, cooled, and the residue dissolved in water and the solution filtered to remove the silica. The sulphate ion was then precipitated by the addition of a solution of barium chloride, the barium sulphate being that obtained from the oxidation of the sulphur dioxide.

(IV) *Purification of Bromine.*

Since practically all bromine contains small amounts of sulphuric acid

and bromine was to be used to oxidize the sulphur dioxide evolved, it was necessary to remove the sulphate from the bromine before using it.

500 grams of ordinary N. F. bromine was washed five times with water in a separatory funnel; then 10 grams of barium hydroxide were dissolved in water and added to the bromine in a separatory funnel and shaken for two hours; the bromine was then washed twice with water and poured into a long necked distilling flask containing 50 cc. of water.

The top of the distilling flask was closed with a glass stopper packed with asbestos, and the side arm extended into a Liebig condenser through an asbestos plug, the bromine being collected in a flask surrounded with ice water. The first part of the distillate and a small amount of bromine remaining in the distilling flask at the end of the operation were discarded.

The distilling flask was immersed in a water bath kept at a temperature slightly above the boiling point of bromine, and fine capillary tubes sealed near the lower ends were placed within the flask which permited the bromine to distil without bumping.

The bromine prepared according to the above method was tested for presence of sulphates according to Krauch-Merck, 76, and showed no cloudiness within twelve hours.

(V) *Preparation of Sodium Hypobromite.*

The sodium hypobromite was always freshly prepared before using. 30 grams of sodium hydroxide purified by alcohol were dissolved in 200 cc. of water and 5 cc. of the purified bromine added slowly from a pipette.

About 100 cc. were placed in each of the absorption tubes.

(VI) *Blank Experiment.*

Since all sodium hydroxide contains traces of sulphur, it was necessary to determine how much barium sulphate was obtained from the sodium hydroxide alone which was used to make the sodium hypobromite.

30 grams of sodium hydroxide purified by alcohol were dissolved in water and bromine added. The solution was then neutralized with hydrochloric acid and carefully evaporated to dryness, the last stage of which was done on a water bath, and then heated in an air oven for two hours at 120°.

The residue in the beaker after cooling was dissolved in water and the solution filtered to remove any silica. The filtrate was then heated to boiling and a solution of barium chloride added.

The average of three trials was 20 mg. of barium sulphate and this correction has been applied in Trials 6, 7, and 8 in Table XII.

(VII) *Results in Table XI.*

In trials 1 to 12 inclusive bromine water was used to oxidize the sulphur dioxide, while in trials 13 to 15 inclusive alkaline hypobromite was used.

In trials 1 to 10 inclusive, elliptical bulbed absorption tubes were used, while in trials 11 to 15 inclusive, spherical bulbed absorption tubes were used.

The barium sulphate representing the sulphur dioxide was always low.

In order to see if any of the sulphur dioxide was going through the absorption tubes unoxidized, two changes were made:—

(1) Spherical bulbed absorption tubes were substituted for the elliptical bulbed ones in order to increase the time of the gas through the oxidizing solution.

(2) The alkaline hypobromite was substituted for the bromine water, for, if any of the sulphur dioxide were converted to sulphur trioxide by

TABLE XI

Trial.	Time of boiling. Hrs.	Barium tetrathionate used. Gm.	$BaSO_4$ from direct decomposition of Ba tet. Gm.	$BaSO_4$ from oxidation of SO_2. Gm.	$BaSO_4$ from oxidation of S. Gm.	Ratios found to a $BaSO_4$ basis. $BaSO_4$: SO_2: S.
A. Bromine water used in elliptical bulbed absorption tubes.						
1	4	1.0000	0.2812	0.2040	0.3239	1:.727:1.15
2	6.5	1.0000	0.3258	0.2715	0.4105	1:.832:1.26
3	7.75	1.0000	0.4113	0.3065	0.5211	1:.742:1.26
4	8.3	1.0000	0.4734	0.4548	0.6573	1:.960:1.39
5	8	1.0000	0.4676	0.3916	0.6311	1:.837:1.349
6	8	1.0000	0.4146	0.3290	0.5850	1:.796:1.418
7	7	0.5000	0.1435	0.1208	0.1297	1:.840:.903
8	9	1.0000	0.3350	0.2614	0.3422	1:.783:1.028
9	9	1.0000	0.3700	0.2746	0.4378	1:.746:1.189
10	7.75	1.0000	0.3500	0.2685	0.3748	1:.767:1.067
B. Bromine water used in spherical bulbed absorption tubes.						
11	7.75	1.0000	0.3347	0.2559	0.3750	1:.765:1.118
12	8.75	1.0000	0.3536	0.2692	0.4095	1:.761:1.157
C. Alkaline hypobromite used in spherical bulbed absorption tubes.						
13	7.75	1.0000	0.3569	0.3355	0.4171	1:.940:1.168
14	7	1.0000	0.5111	0.3518	0.7496	1:.688:1.464
15	7.5	1.0000	0.4160	0.3136	0.5261	1:.754:1.265

the catalytic action of the carbon dioxide (Bigelow, *Zeitschr. phys. Chem.*, **26,** 531 (1898)); (Tithoff, *Zeitschr. phys. Chem.*, **45,** 679 (1903)) the sulphur trioxide would be retained by the excess of sodium hydroxide. Further, the excess of sodium hydroxide reacts with the carbon dioxide reducing the size of the bubbles of gas and thus increases the efficiency of oxidation.

The results of Table XI do not show that the barium tetrathionate solution decomposes according to the equation

$$BaS_4O_6 = BaSO_4 + SO_2 + 2S$$

The barium sulphate was chosen as the basis to obtain the ratios given since it was the least variable.

For example, the ratios of Trial 15 were obtained as shown below, while all the others were obtained in a similar way.

.4160 ÷ 233.44 = .001781	1.781 ÷ 1.781 = 1 $BaSO_4$
.0861 ÷ 64.07 = .001344	1.344 ÷ 1.781 = .754 SO_2
.0723 ÷ 32.07 = .002253	2.253 ÷ 1.781 = 1.265 S

QUANTITATIVE DECOMPOSITION INCLUDING THE ANALYSIS OF THE FILTRATE

As already stated, the results given in Table XI do not show that barium tetrathionate decomposes from a boiling solution according to the equation given above.

Since the amounts of sulphur dioxide and sulphur were always low and somewhat variable, it seemed possible that the above reaction takes place and that the sulphur dioxide and the sulphur react with the thionate in the solution. In order to show this, it was necessary to analyze the filtrate obtained after filtering off the barium sulphate and sulphur which were obtained by boiling the barium tetrathionate solution.

The filtrate was analyzed by the addition of liquid bromine to the solution and keeping the solution warm for three hours. All the barium was precipitated as barium sulphate, and all the remaining sulphur was oxidized to sulphuric acid. The excess of bromine was removed by boiling the barium sulphate filtered off and weighed, and the sulphate ion precipitated by the addition of a solution of barium chloride.

The headings used in Table XII are as follows:—

"$BaSO_4$ From Decomposition of Barium Tetrathionate" means the total barium sulphate obtained by boiling the barium tetrathionate, and includes the barium sulphate obtained by the direct decomposition, the

barium sulphate from the sulphur dioxide, and the barium sulphate from the sulphur.

"$BaSO_4$ From Filtrate" is divided into two parts, for when oxidized with the bromine, barium sulphates separated out directly and all the remaining sulphur was oxidized to sulphuric acid.

"$BaSO_4$ Found From Same Amount of Barium Tetrathionate" means that the same weight of hydrous barium tetrathionate was taken as that used in the decomposition flask, dissolved in water in a beaker and oxidized with bromine. The total weight of barium sulphate obtained in this way was always slightly less than the theoretical calculated from the weight of hydrous barium tetrathionate taken.

Trial 1, Table XII, was the same decomposition as Trial 8 in Table XI; Trial 2 in Table XII the same as Trial 9 in Table XI and etc.

TABLE XII

Trial.	Barium tetra thionate used. Gm.	$BaSO_4$ from decomposition of Ba. Tet. Gm.	$BaSO_4$ from filtrate $BaSO_4$ from direct decomposition. Gm.	$BaSO_4$ from filtrate $BaSO_4$ from all remaining sulphur. Gm.	Total $BaSO_4$ found in analyses.	Total amt. of $BaSO_4$ found rom same famt. of Ba. Tet. Gm.	Error in $BaSO_4$. Gm.
	A. Bromine water used in elliptical bulbed absorption tubes.						
1	1.0000	0.9386	0.2326	1.0500	2.2206	2.2976	−0.0770
2	1.0000	1.0824	0.1972	0.9605	2.2401	2.2976	−0.0575
3	1.0000	0.9933	0.2276	1.0233	2.2447	2.2976	−0.0529
	B. Bromine water used in spherical bulbed absorption tubes.						
4	1.0000	0.9656	0.2383	1.0442	2.2431	2.2976	−0.0495
5	1.0000	1.0323	0.2279	1.0070	2.2672	2.2976	−0.0304
	C. Alkaline hypobromite used in spherical bulbed absorption tubes.						
6	1.0000	1.1095	0.2215	1.0185	2.3495	2.2976	+0.0519
7	1.0000	1.6135	0.0743	0.6722	2.3595	2.3208	+0.0387
8	1.0000	1.2557	0.1668	0.8714	2.2939	2.3208	−0.0269

The results in Table XII show that the loss in sulphur dioxide and sulphur in the boiling solution was recovered in the filtrate, thus proving that secondary reactions occur in the solution during the boiling.

Suppose the results of Trial 5 in Table XII be taken (These results were from the filtrate in Trial 12 in Table XI).

As previously stated, when the filtrate was oxidized by liquid bromine all the barium was precipitated as barium sulphate and the remaining sulphur was oxidized to sulphuric acid. If the barium sulphate, which

is formed directly when the bromine was added to the filtrate, be filtered from the sulphuric acid and weighed, it is possible to get an idea of the total weight of barium sulphate that should be obtained from the filtrate.

For example:—if all the barium were present as tetrathionate,

$0.2279 \times 4 = 0.9116$ gm. of barium sulphate which should be found from the filtrate

if all the barium were present as pentathionate,

$.2279 \times 5 = 1.1395$ gm. of barium sulphate which should be found from the filtrate.

Whereas,

$.2279 + 1.0070 = 1.2349$ gm. of barium sulphate actually found in the filtrate.

From the calculations it may be seen that the weight of the barium sulphate actually found from the filtrate may be accounted for by the assumption that higher thionates than the tetrathionate were formed in the boiling solution.

If the presence of the higher thionates be assumed, they are more stable at the boiling temperature than the tetrathionate which is certainly not in agreement with the generally accepted Mendeleeff (*loc. cit.*) structure.

The presence of colloidal sulphur will not explain the differences found.

CRYSTALLOGRAPHY OF SODIUM AND BARIUM TETRATHIONATES

BIBLIOGRAPHY

No reference was found in the chemical literature where any crystallographic study had been made of the sodium salt.

Curtius, *Jour. f. prak. Ckem.*, N. F. **24,** 225, (1881).

Barium tetrathionate was prepared by completely neutralizing Wackenroder's solution with barium carbonate. The solution was analyzed and the ratio of barium to sulphur was found to be about 1:4.

The salt was also prepared from the solution by the addition of alcohol and crystals $1/2$ cm. long and $1\,1/2$ mm. wide were obtained. The crystals were dried in a desiccator over calcium chloride.

The crystals were observed through the polarizing microscope and were found to be rhombic of apparently hemimorphic habits and possessed a very definite cleavage parallel to the macro and brachypinacoid.

Shaw, *Jour. Chem. Soc.*, **43,** 351, (1883).

Potassium tetrathionate and pentathionate were prepared from Wackenroder's

solution by neutralizing with potassium hydroxide, concentrating on a water bath, and then placed in a vacuum over sulphuric acid and fractionally crystallized. The first and second crops of crystals showed the ratio of potassium to sulphur to be 2:4; the third, fourth and fifth, 2:4.6; the sixth (selected) 2:5.

The potassium tetrathionate crystals when examined under the microscope proved to be hemimorphic forms belonging to the orthorhombic system.

Curtius and Henkel, (*loc. cit.*).

Barium tetrathionate was prepared as previously described. It had a fine silvery texture with well formed crystal plates. When the crystals were examined with polarized light they were found to be monoclinic in nature and almost always twinned.

Fock and Kluss, *Ber.*, 2428, (1890).

Potassium tetrathionate was prepared by the gradual addition of iodine to a concentrated solution of potassium thiosulphate. The separated salt was washed free of potassium iodide with absolute alcohol, dissolved in warm water, filtered, and the filtrate treated with alcohol. The precipitate consisted of large glistening tabular crystals.

The salt was analyzed by oxidizing a known amount in solution with bromine water, and precipitated with barium chloride. Also, a known amount of the salt was heated and the sulphate determined. These analyses show the salt to be $K_2S_4O_6$.

A crystallographic study of the above crystals was made and they were found to be identical with those described by Rammelsberg (*Krys. Phys. Chem.* I, 495) and who gave the composition of the crystalline salt as $K_2S_5O_6$. (Rammelsberg's salt was prepared from Wackenroder's solution).

Potassium tetrathionate crystallizes in peculiar hemimorphic or hemihedral forms belonging to the monoclinic (monosymmetric) system, and not to the rhombic system as stated by Shaw (*loc. cit.*).

Potassium pentathionate was prepared according to the method of Debus (*loc. cit.* 294). The salt on analysis proved to be $2K_2S_5O_6.3H_2O$. They made a crystallographic study of this salt.

EXPERIMENTAL

(I) *Sodium Tetrathionate.*

(1) Crystallization from Absolute Alcohol-Ether.

The crystals were obtained by adding a saturated water solution of sodium tetrathionate at 50° to 60° to an absolute alcohol-ether mixture and allowing it to stand for twelve hours. The crystals thus obtained were very small and occur in aggregate. The widths of the crystal aggregates varied from .006 mm. to .03 mm., while the widths of the individual crystals varied from .001 mm. to .01 mm. The lengths of the aggregates and individual crystals were from two to four times their widths.

(2) Crystallization from Water.

The crystals were obtained from a saturated water solution of sodium tetrathionate at 50° to 60° and cooling with a mixture of salt and ice for about two hours; they were much larger than those obtained from the absolute alcohol-ether solution and they did not occur in aggregates.

The crystals obtained from the water solution varied from .06 mm. to .3 mm. in width, while their lengths were about two to four times as great.

(3) Optical Characteristics of the Crystals.

Fig. 3.—Highly magnified twin crystal of $Na_2S_4O_6.2H_2O$ showing emergence of Bxo = $\mathfrak{a}$ on side pinacoid.

The crystals obtained from the water solution (See Fig. 3) were examined under the polarizing microscope and the following results obtained:—probably monoclinic; generally twinned, both penetration and contact, sometimes showing a more or less hour glass structure; the crystals show on the side pinacoid the normal emergence of Bxo = $\mathfrak{a}$; the acute bisectrix $\mathfrak{c}$ is almost parallel to the trace of one of the small faces which is inclined at an angle of about forty degrees from the direction of elongation; adjacent twins have a difference in extinction of about two to four degrees; $\mathfrak{a} = 1.53 \pm .005$; $\mathfrak{c} = 1.65 \pm .005$; birefringence = .12 (high); 2 V is small, about ten to twenty degrees. The optical sign is +. The edges of the crystals were somewhat rounded which prevented accurate measurement of angles between the traces of crystallographic faces.

(II) *Barium Tetrathionate.*

(1) Crystallization from Absolute Alcohol-Ether.

The crystals from the absolute alcohol-ether mixture were obtained by adding a saturated water solution of barium tetrathionate at room temperature to an absolute alcohol-ether mixture and allowing to stand for twelve hours. The crystals were rod or needle shaped, and the large ones varied in width from .003 mm. to .007 mm. and in length from .01 mm. to .045 mm.

(2) Crystallization from Water.

The crystals were obtained by cooling a saturated water solution of barium tetrathionate at room temperature by means of liquid air. The

dimensions of the crystals were from two to five times those obtained from the absolute alcohol-ether mixture.

(3) Optical Characteristics of Crystals.

The crystals obtained from the water solution were examined under the polarizing microscope and the following results obtained:—rod shaped, probably monoclinic; inclined extinction, angle large, 30°; crystals invariably twinned, contact and frequently polysynthetically; elongation negative; $a = 1.61 \pm .005$; $c = 1.70 \pm .005$; birefringence = .09.

ZINC TETRATHIONATE

BIBLIOGRAPHY

Fordos and Gelis, *Ann. chim. phys.*, (3) **6,** 492, (1842).
Jour. f. prak. Chem., **28,** 478, (1843).

Zinc tetrathionate was prepared by mixing solutions of barium tetrathionate and zinc sulphate and filtering. They further state that the zinc tetrathionate may be obtained from the solution either by evaporation or by the addition of alcohol.

Curtius, *Jour. f. prak. Chem.*, N. F. **24,** 237, (1881).

A tetrathionate of zinc was prepared from Wackenroder's solution and zinc carbonate.

To Wackenroder's solution, previoulsy filtered to remove sulphur, freshly precipitated zinc carbonate was added to neutralization. To this a volume of Wackenroder's solution equal to that already used was added and the solution filtered. A small amount of the solution was boiled in a small tube and it decomposed explosively into zinc sulphate, sulphur, and sulphur dioxide.

The salt was obtained from the solution by evaporating to a syrupy liquid on a water bath at a low temperature for several days, then placing it in a vacuum and further concentrating to a crystalline mass which was separated from the mother liquor and dried between filter papers. The formula of the salt was not stated.

Curtius and Henkel, *Jour. f. prak. Chem.*, N. F. **37,** 147, (1888).

Acid tetrathionate of zinc was prepared from Wackenroder's solution and zinc carbonate.

A definite volume of clear Wackenroder's solution was neutralized with zinc carbonate, and to this a second volume of Wackenroder's solution equal to the first was added. The solution was evaporated in a vacuum and the crystalline residue obtained separated by filtration, and recrystallized from absolute alcohol by evaporation in a vacuum. The salt was dried over sulphuric acid.

Analysis:—A definite weight of the salt was dissolved in water, sodium carbonate added, and chlorine passed through the solution. The zinc was determined as the oxide. The sulphur was precipitated as the sulphate by the addition of barium chloride. The water of crystallization was determined by combustion with lead chromate. The analysis showed the salt to have the composition $Zn(HS_4O_6)_2$.

PREPARATION

(I) *Previous Methods Used.*

Zinc tetrathionate was first prepared by Fordos and Gelis (*loc. cit.*). The general methods used for its preparation are as follows:—

(1) By the action of zinc sulphate on barium tetrathionate. Fordos and Gelis (*loc. cit.*).

(2) By half neutralizing Wackenroder's solution with zinc carbonate. Curtius (*loc. cit.*); Curtius and Henkel, (*loc. cit.*).

The salt prepared by the above investigators in (2) was stated to be the acid salt and in solution reacted strongly acid.

(II) *General Procedure of Method Used.*

Zinc tetrathionate was prepared in solution by the method of Fordos and Gelis, *viz.* by mixing in solution equivalent amounts of zinc sulphate and barium tetrathionate, and filtering off the barium sulphate formed.

$BaS_4O_6.2H_2O$ and $ZnSO_4.7H_2O$ were weighed out in such equivalent amounts as to have 1.0000 gm. of ZnS_4O_6 in solution. They were placed in separate beakers, dissolved in small amounts of water and the zinc sulphate solution added quantitatively to the solution of barium tetrathionate and allowed to stand for a short time. It was then filtered through a Gooch into a test tube within a liter Erlenmeyer filtering flask, using a little suction. This solution was neutral to litmus.

(III) *Preparation of Barium Tetrathionate.*

The barium tetrathionate was prepared according to the "Suggested Method under 'Barium Tetrathionate.' "

(IV) *Preparation of Zinc Sulphate.*

Baker and Adamson's C. P. zinc sulphate was dissolved in warm water at about 35° until a nearly saturated solution was obtained and then filtered. The filtrate was placed in a crystallizing dish and allowed to cool, during which some of the salt crystallized out. The solution was again filtered, the crystallized salt being discarded, and the filtrate placed in a crystallizing dish, seeded with a small amount of very finely pulverized zinc sulphate and allowed to stand for several days. The very small crystals which formed were filtered off, dried between filter paper thor-

oughly ground in a mortar and placed in a glass stoppered bottle. The mother liquor was discarded.

QUALITATIVE DECOMPOSITION

1 gram of ZnS_4O_6 was prepared in solution as previously described and transferred to an Erlenmeyer flask in such a way that there were 100 cc. of solution.

The Erlenmeyer flask was attached to a Liebig condenser and the solution boiled for 24 hours, carbon dioxide being passed through the solution during the entire time. Considerable sulphur collected in the condenser during the process.

The odor of sulphur dioxide was easily detected at the mouth of the condenser. The evolved gas was passed into bromine water, the excess of bromine boiled off, a few drops of hydrochloric acid added and then a solution of barium chloride. A white precipitate was formed.

Negative results were obtained for hydrogen sulphide when tested for with lead acetate.

At the end of the boiling the residue in the condenser was added to the flask, the solution filtered, and the residue and filtrate tested qualitatively.

(I) *Residue.*

It was found to consist of sulphur, sulphide being absent.

(II) *Filtrate.*

(1) Sulphate:—The solution was tested in the usual way and found present.

(2) Thiosulphate:—

(a) Tested with a solution of ammonium molybdate and concentrated sulphuric acid. Blue ring immediately.

(b) Tested with iodine solution. 1 drop of N/10 iodine was decolorized by 10 cc. of the solution; two drops gave an iodine color.

(c) Tested with a dilute solution of potassium permanganate. The solution was bleached.

(3) Sulphite:—The sodium nitroprusside-potassium ferrocyanide-zinc sulphate tested gave a negative result.

(4) Trithionate:—The mercuric chloride, potassium permanganate, mercurous nitrate, and hydrochloric acid tests were applied. Definite results were not obtained, but if present it was in very small amounts.

(5) Pentathionate.

(a) Tested with ammoniacal silver nitrate. Immediate brown precipitate.

(b) Tested with concentrated potassium hydroxide. Cloudiness which does not disappear when made slightly acid with hydrochloric acid.

(c) Tested with mercurous nitrate. Black precipitate at first, but on further addition of the mercurous nitrate the precipitate became yellow.

From the results of the tests given above it may be concluded that the following are the final products of decomposition in a boiling solution of zinc tetrathionate:—sulphate, sulphur dioxide, sulphur and some pentathionate; also a small amount of thiosulphate.

QUANTITATIVE DECOMPOSITION

(I) *Descriptive.*

The apparatus used, the time of boiling, and the passing of the carbon dioxide, were the same as under barium.

The absorption tubes for the sulphur dioxide were spherical bulbed; alkaline hypobromite, which was prepared as previously described under barium, was used as the oxidizing agent.

(II) *Procedure.*

1.0000 gm. of zinc tetrathionate was prepared in solution as described under "General Procedure of Method Used," transferred quantitatively to the Erlenmeyer decomposition flask in such a way that the total volume of water used was 100 cc.

At the end of the boiling the sulphur which had collected in the condenser was removed to the decomposition flask, and the solution filtered through a hard filter using all necessary precautions.

(1) The Residue.

The residue on the filter was washed into a beaker and oxidized by addition of bromine using the precautions to obtain and oxidize all the sulphur. After the removal of the excess of bromine, the sulphate ion was precipitated by the addition of a solution of barium chloride using the necessary precautions, and the barium sulphate obtained is designated in the tabel as "$BaSO_4$ From Oxidation of Sulphur."

(2) The Filtrate.

The filtrate obtained after the removal of sulphur was heated nearly

to boiling and a solution of barium chloride used, thus precipitating the sulphate ions present. The barium sulphate formed was filtered off and is designated in the table as "$BaSO_4$ From Zinc Sulphate."

The contamination due to the presence of zinc ions as determined by dissolving the barium sulphate in hot concentrated sulphuric acid and reprecipitating by diluting with water amounted to only about 1 mg. and in most of the determinations has been neglected.

(3) Sulphur Dioxide.

Sulphur dioxide was determined exactly as described under barium.

The sulphur content of the sodium hydroxide as found in the blank experiment under barium has been applied in each determination.

TABLE XIII

Trial.	Time of boiling hrs.	Zinc tetrathionate used. Gm.	$BaSO_4$ from zinc sulphate Gm.	$BaSO_4$ from oxidation of sulphur dioxide. Gm.	$BaSO_4$ from oxidation of sulphur. Gm.	Ratios found to $ZnSO_4$ basis $ZnSO_4$: SO_2: S.
1	8	1.0000	0.2426	0.1216	0.2248	1: .501: .927
2	8	1.0000	0.2399	0.1925	0.1811	1: .802: .755
3	9.5	1.0000	0.2344	0.2020	0.2067	1: .860: .881
4	8	1.0000	0.2862	0.2372	0.2302	1: .828: .803
5	8	1.0000	0.2478	0.1987	0.1520	1: .800: .613

The ratios obtained above do not show that zinc tetrathionate in solution decomposes quantitatively into zinc sulphate, sulphur dioxide, and two atoms of sulphur.

The ratios given in the above table were obtained in exactly the same way as under Barium in Table XI, except the "Barium Sulphate From the Zinc Sulphate" has been converted to an equivalent amount of zinc sulphate.

QUANTITATIVE DECOMPOSITION INCLUDING THE ANALYSIS OF FILTRATES

As in the case of barium, the boiled solution after the removal of the sulphur and the sulphate ions was oxidized with bromine, the excess of bromine boiled off and a solution of barium chloride added observing the necessary precautions.

The headings in Table XIV are as follows:

"$BaSO_4$ From Decomposition of Zinc Tetrathionate" means, after the solution of zinc tetrathionate has been boiled, it is the total barium sulphate obtained from the zinc sulphate, plus that obtained from the oxidized sulphur dioxide, plus that from the oxidized sulphur.

"$BaSO_4$ From Filtrate" means the final filtrate which was oxidized with bromine and precipitated with a solution of barium chloride in the usual way.

"Total Amount of $BaSO_4$ From Same Amount of Zinc Tetrathionate" means that 1.0000 gm. of zinc tetrathionate was prepared in solution, using the same samples and the same amounts of barium tetrathionate and zinc sulphate as were used to prepare the zinc tetrathionate in the decomposition flask, oxidized by bromine and precipitated by a solution of barium chloride observing precautions previously stated.

TABLE XIV

Trial.	Time of boiling. hrs.	Zinc tetrathionate used. Gm.	$BaSO_4$ from decomposition of zinc tetrathionate. Gm.	$BaSO_4$ from filtrate. Gm.	Total $BaSO_4$ found in analyses. Gm.	Total amt. of $BaSO_4$ from same weight of zinc tetrathionate. Gm.	Error in $BaSO_4$. Gm.
1	8	1.0000	0.5890	2.5013	3.0903	3.0386	+0.0517
2	9.5	1.0000	0.6431	2.4404	3.0835	3.0386	+0.0449
3	8	1.0000	0.7536	2.2458	2.9994	3.0755	−0.0761
4	8	1.0000	0.5985	2.4325	3.0310	3.0755	−0.0445

The results of Table XIV show that the loss of sulphur dioxide and sulphur in the decomposition of the zinc tetrathionate by boiling was recovered in the filtrate.

The ratio of zinc sulphate to sulphur dioxide in Table XIII is about the same as barium sulphate to sulphur dioxide in Table XI, while the ratio of zinc sulphate to sulphur in Table XIII is less than that of barium sulphate to sulphur in Table XI.

If there was good evidence of the formation of pentathionate and quite probably hexathionate when the barium tetrathionate solution was boiled, there is stronger evidence that the higher thionates were formed when the zinc tetrathionate solution was boiled, because there was a proportionately greater loss of sulphur from the boiling solution.

NICKEL TETRATHIONATE

BIBLIOGRAPHY

Kessler, *Jour. f. prak. Chem., loc. cit.*, 36.
Pogg. Ann. Phys. Chem., loc. cit., 256.

"Nickel tetrathionate was prepared by mixing equivalent solutions of nickel sulphate and lead tetrathionate and evaporating in a vacuum. The salt was very deliquescent and its solution was practically as stable as solutions of tetrathionic acid."

The analysis of the salt was not given.

PREPARATION

(I) *General Procedure of Method Used.*

Nickel tetrathionate was prepared in solution in a way similar to that used in the case of the zinc.

2.000 gm. of $BaS_4O_6.2H_2O$ and 1.322 gm. of $NiSO_4.6H_2O$ were weighed out, placed in separate beakers and each dissolved in a small amount of water. The nickel sulphate solution was then transferred quantitatively to the barium tetrathionate solution, allowed to stand a short time and filtered exactly as under zinc.

The solution had a light green color and was neutral to litmus.

(II) *The Barium Tetrathionate and Nickel Sulphate Used.*

The same sample of barium tetrathionate was used as in the case of zinc. Ordinary C. P. hydrous nickel sulphate was used.

QUALITATIVE DECOMPOSITION

The nickel tetrathionate solution was prepared as described and transferred to the Erlenmeyer decomposition flask so that there were 100 cc. of water used. The apparatus and procedure were the same as described under zinc.

The solution was boiled for 24 hours and during this time the color remained a light green, thus showing that hydrogen sulphide was not evolved and nickel sulphide formed.

During the boiling, sulphur dioxide was given off and sulphur collected in the condenser. At the end of the boiling the sulphur in the condenser was removed to the decomposition flask and the solution filtered.

(I) *Residue.*

The residue proved to be sulphur.

(II) *Filtrate.*

Tests were made for sulphate, thiosulphate, sulphite, trithionate, and pentathionate and the results show the final products in the decomposition of a boiling solution of zinc tetrathionate are:—sulphate, sulphur dioxide, and sulphur; some pentathionate and a small amount of thiosulphate.

CONCLUSIONS

Sodium Tetrathionate.

(1) Sodium tetrathionate was prepared by several similar methods

and the salt crystallized from water solution by cooling had the highest degree of purity.

(2) The salt crystallized from water solution had the composition $Na_2S_4O_6 . 2H_2O$.

(3) The yield was considerably increased by preparing the salt according to the "Suggested Method."

(4) The dissociation pressure of the hydrous sodium tetrathionate is of such magnitude that the salt should not be dried over concentrated sulphuric acid for any considerable time.

Barium Tetrathionate.

(1) Barium tetrathionate was prepared and on analysis proved to be quite pure, and that crystallized from a water solution had the highest degree of purity.

(2) Practically all the details of the method for its preparation were worked out.

(3) Barium tetrathionate slowly decomposes at the ordinary temperature.

(4) Qualitative decomposition of a boiling solution showed that the final products were sulphate, sulphur dioxide, and sulphur together with pentathionate and a trace of thiosulphate.

(5) Quantitative decomposition of the boiling solution showed that secondary reactions occur in the solution forming higher thionates.

CRYSTALLOGRAPHIC STUDY OF SODIUM AND BARIUM TETRATHIONATE

(1) Crystals of both sodium and barium tetrathionates were prepared from a water solution and some of their optical characteristics determined.

Zinc Tetrathionate

(1) A solution of zinc tetrathionate was prepared and it was neutral to litmus.

(2) Qualitative decomposition of the boiling solution showed that the final products were sulphate, sulphur dioxide, sulphur and some pentathionate together with small amount of thiosulphate.

(3) Quantitative analysis of the boiling solution showed that secondary reactions occur and that higher thionates were formed to a greater extent than in the case of barium.

Nickel Tetrathionate

(1) A solution of nickel tetrathionate was prepared; it had a light green color and was neutral to litmus.

(2) Qualitative decomposition of the boiling solution showed that the final products were sulphate, sulphur dioxide, sulphur and some pentathionate together with a small amount of thiosulphate.

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